THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

SEPTEMBER, 1927.

XXXVIII. *The Physical and Biological Effects of High-frequency Sound-waves of Great Intensity.*

By Prof. R. W. Wood, *For.Mem.R.S.*, *and* Alfred L. Loomis*. (Communication No. 1 from the Alfred Lee Loomis Laboratory, Tuxedo, N.Y.)

[Plates VII.—XIII.]

Introduction.

In the present paper we shall give an account of a preliminary survey of what appears to be a wide field for investigation, opened up by the study of the very surprising and remarkable effects obtained with sound-waves of high frequency and great intensity generated in an oil-bath by a piezo-electric oscillator of quartz operated at 50,000 volts and vibrating 300,000 times per second.

The radiation pressure exerted against a glass disk 8 cm. in diameter amounts, under certain circumstances, to 150 grams, and when operating against the free surface of the oil (from which the radiation is totally reflected) raises it in a mound 7 cm. in height, surmounted by a fountain of oil drops, some of which are projected to an elevation of 30 or 40 cm.

The waves can be transmitted along a glass thread 0·2 mm. in diameter and a metre or more in length, and the end of the thread, if squeezed between the thumb and finger, burns a groove in the skin. A tapering glass rod, 0·5 mm. in diameter at the tip, can be thrown into vibration of such

* Communicated by the Authors.

ntensity that a pine chip smokes and emits sparks when pressed against the tip, the rod burning its way rapidly through the wood, leaving a hole with blackened edges. If a glass plate is substituted for the chip, the rod drills its way through the plate, throwing out the displaced material in the form of a fine powder or minute fused globules of glass.

If the waves are passed across the boundary separating two liquids such as oil and water or mercury and water, more or less stable emulsions are formed. Chemical reactions are accelerated, crystallizations started, and other remarkable effects produced by these very intense super-sonic vibrations.

Preliminary experiments with interference fringes formed between a vibrating plate and one at rest indicate that the amplitude of the vibration is of the order of magnitude of a wave-length of light, yet an enormous amount of energy is delivered. The mean energy and acceleration are both proportional to the square of the frequency, and we are here dealing with what Prof. C. V. Boys very tersely describes as "*All* acceleration and *no* motion."

The method employed in the generation of the waves is essentially the one developed by Professor Langevin in 1917 for the purpose of locating submarines by the echo of a narrow beam of high-frequency sound-waves. Shortly thereafter experiments along similar lines were inaugurated by the British and American navies.

In Langevin's original apparatus the vibrations of the piezo-electric quartz plate were excited by a Poulsen arc in connexion with suitable condensers and coils. Voltages as high as thirty or forty thousand were applied to the plates, and the amplitude of the waves raised to such a degree that small fish were killed by the radiation and pain of considerable severity was experienced when the hand was thrust into the water in the tank. The Poulsen arc proved troublesome, however, owing to its instability, which made it impossible to keep the electrical vibration in tune with the natural frequency of the quartz plate, and it was speedily supplanted by the vacuum tube, which is used exclusively at the present time.

Since the coefficient of viscosity increases with the square of the frequency, comparatively low frequencies only can be employed when beams of sound are to be projected under water over long distances for signalling or other purposes. Voltages of one or two thousand at frequencies of from 30 to 40 thousand are used for the most part in work of this nature.

In our experiments this limitation is not imposed, since

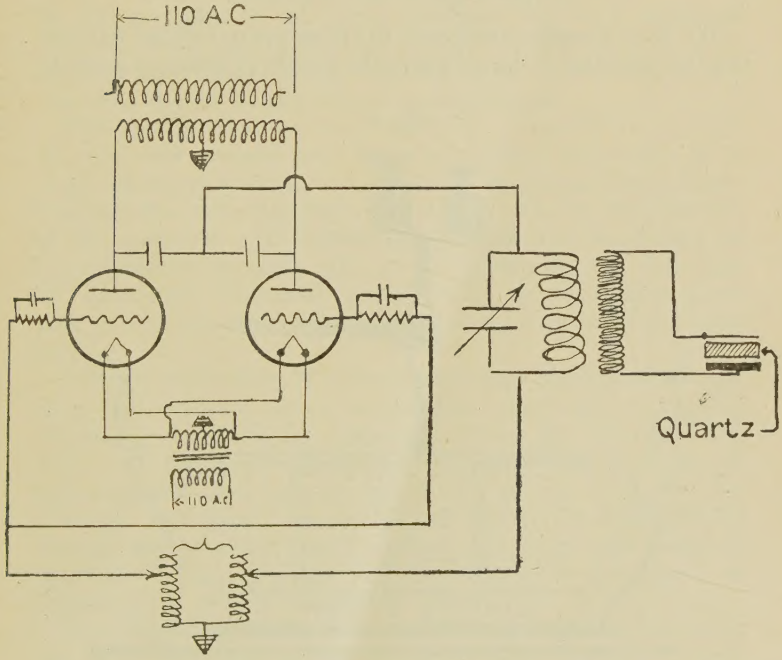
absorption of the radiation by the medium does not interfere to any great degree with the study of effects close to the source, and we operate usually with voltages in the vicinity of 50,000 at frequencies ranging from 200,000 to 500,000.

Description of the Apparatus.

(See Plate VII. fig. 1.)

The apparatus employed in the present work was built in the Research Laboratory of the General Electric Co. at

Fig. 1.



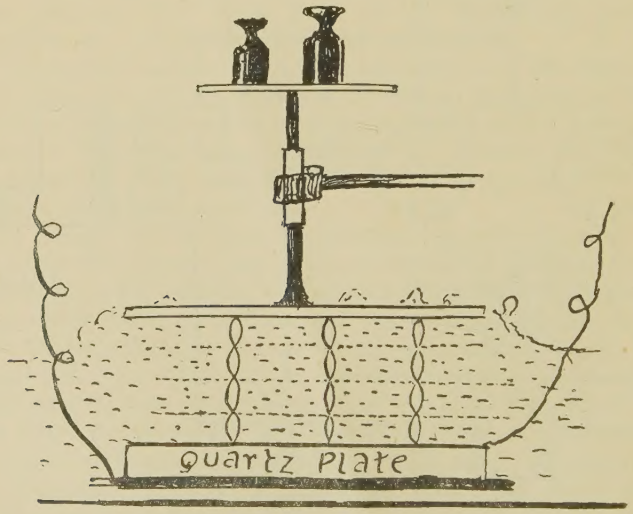
Schenectady. It consists of a two kilowatt oscillator, designed originally for an induction furnace, a bank of oil condensers, giving capacities up to 0·1 microfarad, a large variable air condenser, and several pairs of coaxial coils for raising the voltage. The primary or outer coil consisted of from 7 to 20 turns of Litzendraht cable, the coils varying from 16 to 24 cm. in diameter. The secondary coils were wound on glass cylinders (100 to 250 turns) and mounted within the primaries. Fig. 1 shows in conventional manner the wiring of the various parts. The use of several coils was

found to be necessary as we employed quartz plates varying in thickness from 7 to 14 mm., with which we obtained waves with frequencies ranging from 100,000 to 700,000 cycles per second. The quartz plates were circular disks, and when in operation, one of them rested on a disk of sheet lead at the bottom of a dish of transformer oil. The other electrode consisted of a disk of very thin sheet brass resting on the upper surface of the quartz. The coils for raising the potential and the glass dish with oil, in which the quartz oscillator is immersed, are shown on Plate VIII.

Pressure due to the Radiation.

We have already mentioned the pressure developed against the free surface of the oil above the quartz vibrator as a result

Fig. 2.



of the reflexion of the radiation. In the case of reflexion from plates of glass or metal the magnitude of the effect can be measured. We found that a glass disk 8 cm. in diameter attached to a glass rod and supported as shown in fig. 2 would support a weight of 150 grams. The pressure is a maximum when the distance between the under surface of the plate and the upper surface of the quartz oscillator is a whole number of half wave-lengths. Under this condition the reflected wave strikes the oscillator when its phase is such as to reflect the wave back to the plate. The energy is thus imprisoned

by multiple reflexions between the vibrator and the plate, and the amplitude rises to a very high value, for the same reason that the amplitude of vibration of the stationary waves on a thread attached to a vibrating tuning-fork may be twenty or thirty times the amplitude of the fork when the length of the thread is properly adjusted.

If the rod which supports the glass plate is held in the fingers and the plate pushed down gradually into the oil a strong resistance is encountered periodically, as if the plate were breaking its way through a series of resisting films. In the positions of maximum pressure the energy is reflected back and forth between the oscillator and plate. In the positions of minimum pressure the wave reflected down from the plate meets the oscillator when it is in such a phase as to transmit the reflected wave. That such is the case was shown by the following experiment.

The quartz oscillator was mounted vertically in a large oil bath and a metal vane hung by a bifilar suspension at a short distance to one side of it. With the oscillator functioning, this vane was deflected to one side by the pressure of the radiation. If now a glass plate was immersed in the oil on the opposite side of the oscillator, the deflexion of the vane increased periodically as the glass plate was moved towards the oscillator, *i. e.* it swung back and forth.

This shows us that, to get the maximum amount of energy from the oil into a bath of some other liquid (or into a solid) immersed in the oil, the distance between the bottom of the bath and the upper surface of the oscillator must be so adjusted that the energy builds up between the two by multiple reflexions. A beaker of water, for example, is heated much more rapidly when the above condition is fulfilled. This operation will be referred to in future as adjusting for energy density.

The height of the oil mound raised above the surface over the plate depends in the same way upon the depth of the oil. We have never obtained a smooth uniform mound, as might be expected with low amplitude if the plate were simply expanding and contracting as a whole. With the oscillator operated at low voltage, a number of humps appear on the surface which shift their position with every alteration in the capacity of the condenser. When the frequency of the electrical oscillation is tuned exactly to the natural frequency of the crystal plate the oil mound rises to a height of 7 cm., its summit erupting oil drops like a miniature volcano. Further increase of the power gave a mound 10 cm. in

height, but the quartz plate broke into fragments. A photograph of the oil fountain taken against a very bright background with an exposure of 1/500 second is reproduced on Plate VII. fig. 2.

Stationary waves on tubes

If a glass tube a metre long and 2 or 3 cm. in diameter, closed at the bottom like a test-tube, is coated on the inside with a layer of a heavy oil, the oil gathers itself together in rings about 3 mm. apart, which line the tube from top to bottom, as soon as the lower end is dipped into the vibrating oil over the quartz plate. The rings appeared to be interrupted in places by another system of waves, and a permanent record of the pattern was secured by substituting paraffin, coloured with aniline red, for the oil and using it in a warm tube. A photograph of a portion of the tube with the rings cut across into a pattern of regularly spaced dots is reproduced on Plate IX. fig. 3.

The wave-length of the oblique system is about 1·5 times that of the horizontal system.

We at first attributed the rings to a stationary system of compressional waves formed by interference between disturbances reflected down from the top of the tube with those coming up from below, but the velocity deduced from the wave-length and frequency was much less than the velocity of sound in glass. The waves turned out to be transverse vibrations, the wave-length being but a small fraction of the diameter of the tube. If a similar glass tube was used without the oil, and the outer surface heated to the softening point in the flame of a blast-lamp while the vibrations were running up and down the tube, the stationary system was permanently recorded in the glass, and could be made visible by casting a shadow of the tube with sunlight (or light from any concentrated source) on a sheet of paper held at a distance of 10 or 15 cm. from the tube. A shadow photograph, made in this way, is represented on Plate IX. fig. 4.

We have made no careful study of the modes of vibration of a tube for high frequencies, and have no explanation for the oblique system of greater apparent wave-length. It seems evident, however, that the velocity of propagation is greater for the waves forming this system than for the others. It was observed also, as the tube cooled down, that the paraffin remained fluid longer in those portions of the tube where the double system registered than at other places, indicating that the internal heating of glass was greater here than elsewhere.

Transverse waves on glass plates, rods and threads.

If a glass rod is cemented with sealing-wax to the centre of a circular glass disk, dusted with lycopodium, a beautiful system of concentric circular rings forms on the plate as soon as the lower end of the rod is brought into contact with the vibrating oil-bath.

These rings are formed at the nodal lines of a system of stationary waves in the plate, formed by the interference of the waves reflected from the rim with those radiating from the centre. If the disk is thicker at the centre than at the rim (we used the base and stem of a broken wine-glass) the distance between the rings is less at the rim than at the centre, from which the inference can be drawn that the waves are transverse vibrations, which is to be expected considering the arrangement of the rod and disk. The velocity is higher at the thick than at the thin portions, consequently the rings are further apart.

If the rod is cemented to the disk at a point situated at a small distance from the centre, we obtain the complicated pattern reproduced as a negative (*i. e.* the lycopodium lines black) on Plate X. fig. 5. Here we evidently have the waves reflected from the rim coming to a focus, which becomes a second source of radiation on the side of the centre opposite to the rod, and a system of radiating interference fringes is formed, as with two similar sources of light. The pattern in the immediate vicinity of the sources is of especial interest.

A beautiful system of circular rings of variable spacing is produced by dusting the inner surface of a champagne glass with lycopodium, and touching the base to the surface of the vibrating oil. At the rim the rings are closer together than near the centre, where the glass is thicker.

Applying the lycopodium method to a glass rod which has been drawn down in a flame to a long tapering point, the diameter varying from 7 to 0·5 mm., gives us a system of rings, the separation of which decreases rapidly as we pass from the thick to the thin portion. This shows that the velocity of propagation is a function of the diameter of the rod, which will of course be true for transverse, but not for longitudinal disturbances. If the rod terminates in a fine point no rings are formed, since in this case the reflexion from the end is negligible and the stationary wave system is not formed.

More permanent rings better suited for wave-length measurements were made by the following method. A

small ball of soft red wax was stuck on the point of the rod held vertically over the oil. This melted and slid down the rod as soon as the lower end was dipped in the oil, owing to heat developed by friction between the vibrating glass and the wax. The wax solidifies in rings above the ball as it descends leaving a permanent record of the wave-length, as shown on Plate X. fig. 6.

In this particular case the rod is drawn down from a glass tube closed at the bottom. The energy abstracted from the oil and thrown into the rod is greater than when a large solid rod forms the collector. Remarkable calorific effects obtained with this type of collector will be described presently.

Heat developed at Contact-point between vibrating rods and matter.

This type of heating was first accidentally observed when taking the temperature of the oil in the erupting mound over the vibrator. Though the mercury registered only 25°, the thermometer tube became so hot at the point where it was held between the thumb and finger that it had to be released. The heat of course is developed by friction between the vibrating glass stem and the skin of the fingers, or rather by the rapid *pounding* of the transverse vibrations, and becomes unbearable only when the glass is squeezed tightly between the thumb and finger. This same heating is observed when any object such as a rod, tube, beaker or flask is held by the fingers and dipped into the vibrating oil-bath. If a glass rod is drawn out into a long thread of the diameter of a horsehair, terminating in a pear-shaped bead, the heat developed, when the end of the thread is squeezed between the fingers and the bead dipped into the oil fountain, is so great that a groove with seared edges is left in the skin. A week later bright red spots similar in appearance to blood-blisters developed, which did not disappear for several weeks. These were perhaps due to an effusion of blood from capillaries deep down in the skin, which were ruptured by the vibration. Still more powerful effects were obtained with rods 0·5 mm. in diameter drawn out from the top of an Erlenmeyer flask the neck of which had been closed by fusion in a blast-lamp. Shown at extreme right of Plate VIII., which also shows rack-and-pinion stand for adjusting a flask of water containing a frog for maximum energy density. A side tube was fused to the flask, by which it was supported in a clamp-stand, furnished with a rack-and-pinion movement, by which the distance between the flat bottom of the flask

and the vibrator could be accurately adjusted for the position necessary for securing the maximum density of the radiation imprisoned between the surfaces. With this condition fulfilled a dry pine-chip, pressed against the top of the glass rod, smoked and emitted an occasional spark, while the rod rapidly burned its way through the wood, leaving a hole with charred edges. The heating, of course occurs only at the point of contact, the remainder of the rod being quite cold.

If a plate of glass is pressed lightly against the top of the rod, the surface of the plate is etched at the point of contact, the microscope showing a curious scalloped pattern. If the pressure is increased the rod drills its way rapidly through the plate, and the microscope shows small globules of molten glass, and finely powdered material.

This method of conducting the vibration along threads of glass yields a valuable technique for the investigation of the biological effects of the high-frequency vibration, which can thus be applied at a small point on a living organism, egg or embryo under the microscope. We have felt the heat at the end of a thread a metre long and 0·2 mm. in diameter. With the flask form of collector, with proper adjustment for the system of stationary waves between the top of the quartz vibrator and bottom of the flask, the energy thrown into the glass thread is often so great that the thread breaks into pieces.

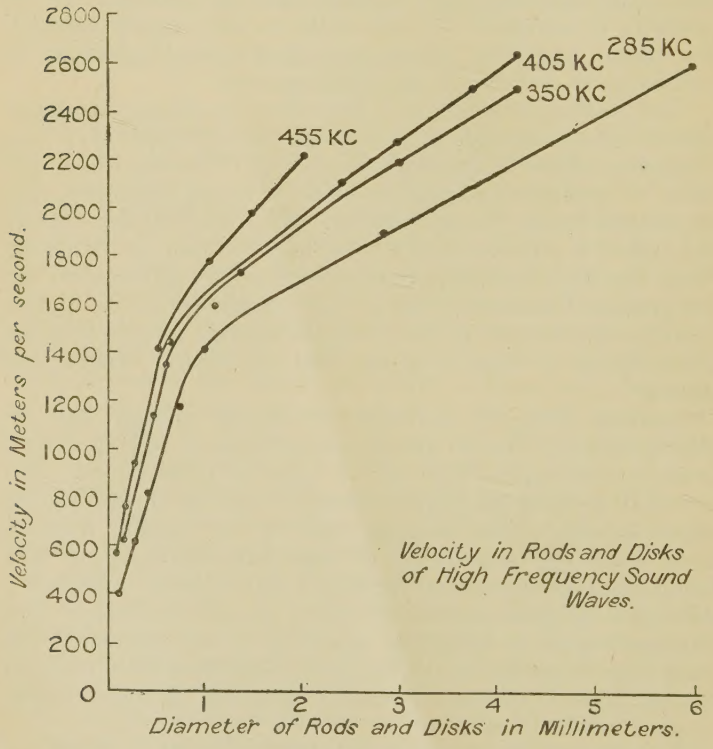
Another form of collector by which energy can be abstracted from the oil and conducted into a rod or thread is shown in fig. 6, Plate X.—a tube of glass closed with a round bottom and drawn down to rod or thread at the opposite end. The sloping wall of the bottom appears to facilitate the production of transverse waves and it was found also, in experimenting with a flat collector made of a thin plate of glass, drawn off into a rod at one corner, that the most vigorous vibrations occurred in the rod when the plate was immersed in the oil in a slightly oblique position and not when it was parallel to the surface of the quartz plate.

Velocity and Dispersion of Transverse Waves in Solids.

By the methods just indicated it is possible to measure the velocity of propagation of the transverse waves if the frequency is known. As has been said, the velocity is a function of the diameter of the rod or the thickness of the plate. Micro-photographs of the rings on rods of 0·15, 0·5 and 1 mm. in diameter are reproduced on Plate XI. fig. 7. Observations made with waves generated by quartz

vibrators of different thicknesses showed that the velocity was also a function of the frequency, as is the case with light traversing a dispersing medium. We investigated the phenomenon of dispersion employing disturbances of four different frequencies—441, 405, 350, and 285 thousand vibrations per second—forming the rings of red wax or lycopodium on rods and threads of glass varying in diameter from 6 mm. to 0·1 mm. The results are shown graphically in the curves reproduced in fig. 3. The velocity, which at

Fig. 3



285 kilocycles is 2600 metres per second in a glass rod 6 mm. in diameter, falls off to 400 metres in the case of a glass thread 0·1 mm. in diameter.

As the diameter of the rod is increased it becomes increasingly difficult to form the rings, and for values of the order of magnitude of the half wave-length it becomes impossible to obtain any record of the transverse waves, even

by the lycopodium method, which is the more sensitive of the two. With very large energy input we several times obtained under these conditions indications of waves of considerably greater wave-length than the transverse ones which we at first believed represented the longitudinal disturbance. Measurements, however, were not in agreement with the known velocity of sound in glass, which is in the neighbourhood of 5000 metres per second.

The dispersion, for a rod of any given diameter, is given by taking the ordinates from the four curves corresponding to the same abscissa, the velocity of propagation increasing with the frequency at first rather rapidly, then more slowly, and finally rapidly again. These values are preliminary only and do not represent a very high degree of accuracy.

Sonic Interferometer and the Velocity of the Waves in Liquids.

Another method was developed for the determination of the velocity in liquids, depending upon the formation of a system of stationary waves between the vibrator and a reflector. We have alluded to the variable periodic pressure exerted upon a plate pushed down through the oil over the vibrator. By counting the number of resisting planes as the plate is lowered through a measured distance, the wave-length can be determined. It is obvious that the accuracy of this method depends upon the precision with which the points of maximum or minimum pressure can be determined. It was found that the best results were secured by employing electrical means for registering the reaction of the reflected waves upon the piezo-electric vibrator, as employed by Professor Pierce of Harvard, and a very compact instrument of low power has been developed in collaboration with Professor J. C. Hubbard, now of Johns Hopkins University, who has already made a series of very satisfactory observations of the velocity of sound in various liquids, solutions, and liquid mixtures. It is possible to obtain results of great accuracy with only a few cubic centimetres of liquid. The results of this work will be reported in a subsequent paper.

As is apparent this method is analogous to the employment of the Fabry and Perot interferometer for determining the wave-length of light, and the apparatus may be termed a Sonic Interferometer. With the plate in the position for maximum pressure, and multiple to-and-fro reflexion of the waves, the condition is similar to that obtaining with a Fabry and Perot instrument illuminated by *parallel rays*

at normal incidence, with its plates at such a distance as to secure the maximum transmission of light. If the wave-length of light or the distance between the plates is slightly altered, the transmission falls to a very low value. Transmission in this case corresponds to the entrance of the energy into a beaker of water tuned for maximum energy density, as previously described. In the usual treatment of the Fabry and Perot interferometer one is apt to overlook the circumstance that under certain conditions transmission of the light is refused, as it is customary to illuminate the instrument by an extended luminous source such as a flame—in which case the amount of light transmitted is independent of wave-length, but transmission is permitted in specified directions only, this limitation giving rise to the rings.

Heating of Liquids and Solids.

The kinematic coefficient of viscosity increases as the square of the frequency. At frequencies from 300 to 400 K.C. the heating of liquids is very pronounced. Thus a test-tube filled with water and immersed in a beaker containing water and cracked ice heats rapidly when the beaker is lowered over the vibrating quartz disk, showing that the energy of the sound-waves (which pass into the water in the test-tube after traversing the intervening glass walls and the ice-water) is converted into heat by absorption, the water in the test-tube rising rapidly in temperature notwithstanding the circumstance that it is surrounded by a layer of water at 0°. The rise of temperature may be as great as one degree every three seconds, the rate depending upon whether the depth of the water and the distance between the vibrator and the bottom of the beaker are adjusted for multiple reflexions of the radiation, as previously described. With 250 c.c. of water the heat developed amounted to about 900 calories per minute—with 150 c.c., 750 cals.; with 100 c.c.; 700 cals.; and with 50 c.c. (in a test-tube) 430 cals.

These results show that though the temperature rise is higher in the case of small volumes of liquid, the total energy abstracted from the radiation increases with the volume of liquid employed.

We have not as yet made any precise determinations of the heating of various liquids by the radiations. Three determinations with 45 c.c. of ethyl alcohol gave 4°·1, 3°·6, and 4°·5 as the temperature elevation for an exposure of 20 seconds. These observations were, however, made

before the necessity of accurate adjustment of the containing vessel had been realized. In work of this nature it will be necessary to devise some method by which it will be possible to throw the same amount (or a measured amount) of energy into the fluids under investigation.

A few observations have also been made of the internal heating of solids. A block of newly formed ice (distilled water frozen in a beaker by ice and salt) was subjected to the action of the sound-waves for two minutes in a beaker of ice water containing numerous small fragments of ice which kept the temperature of the water at 0°. Adjustment for maximum energy density was secured by watching the block of ice which was elevated above its normal position in the water by the radiation pressure. At the end of the exposure the block of ice, on being squeezed between the thumb and fingers, broke up into small fragments showing that liquefaction had taken place throughout the mass, as in the case of so-called "rotten ice" after exposure to the sun's rays.

We found that this experiment could not be duplicated with natural ice (*i. e.* pond ice), and believe that this may be due to the circumstance that in this case we are dealing with a single crystal, whereas in the case of the artificial ice we have a mass of interlocking crystals, the heating taking place at the crystal interfaces.

To eliminate effects due to air bubbles in the ice, distilled water, thoroughly boiled to remove air, and coloured with fluorescein, was covered with a thin layer of paraffin and frozen. The outer portions of the ice block were perfectly transparent, while the central portion was yellowish in colour, somewhat cloudy and devoid of fluorescence, showing that the fluorescein was not in solution. On exposing this block to the radiation for thirty seconds and examining it in sunlight against a black background, it was found to be traversed by innumerable interlacing planes of green fluorescence, caused by the internal melting and consequent solution of the dye. A somewhat analogous effect was noted in one of our earlier experiments, in which a bit of candle (probably stearic acid) was melted on the surface of water in a test-tube and allowed to solidify. Water was then introduced above the solid plug, and the lower end of tube subjected to the vibration. No trace of the radiation appeared in the water above the plug the *under surface* of which melted rapidly and was thrown down into the water as a white emulsion, showing the powerful absorption of the radiation by the solid stearic acid.

It was during an attempt later on to duplicate this experiment with paraffin that we obtained the apparent crystallization of the substance referred to later on in this paper.

Formation of Emulsions and Fogs.

If two non-miscible liquids such as oil and water are simultaneously subjected to the radiation in the same beaker, an emulsion or colloidal solution is formed as a result of the forces acting at the interface between the liquids. This phenomenon was first observed in an earlier arrangement of our apparatus, in which the quartz oscillator operated in a thick layer of oil floating on water. White clouds of finely divided oil were thrown down into the water and occasionally, probably when exact tuning happened to be secured, large masses of oil were projected, with almost explosive violence, down into the water, as a shower of large drops. Stable emulsions resembling milk can be made of stearic acid or paraffin and water. A beaker of water with a layer of mercury at the bottom, under the influence of the vibrations becomes first milky, then brown, and finally black. At the end of twenty-four hours most of the mercury has settled, but a sufficient amount remains in suspension to make the water slightly turbid.

Colloidal solutions of the low melting-point alloys have also been made.

At a liquid-air interface, in the case of less viscous liquids the forces brought into play drive the liquid into the air in the form of a spray of minute droplets, forming a fog. This atomization (to use the popular term) of a liquid by the sound-waves is best shown by pouring a little benzol into a beaker and lowering the beaker into the oil, tuning it for energy density. The beaker fills rapidly with a cloud of white smoke, a benzol fog, the surface of which is in tumultuous motion. A photograph of this phenomenon is reproduced on Plate XII. fig. 10. The beaker was illuminated by sunlight (reflected from a mirror) against a black background, the camera pointing as nearly as possible towards the direction from which the light was coming, to secure the maximum illumination. The filaments rising from the surface are larger droplets moving too rapidly for the camera shutter. Fogs can also be formed over water, but in this case the droplets are larger and settle rapidly.

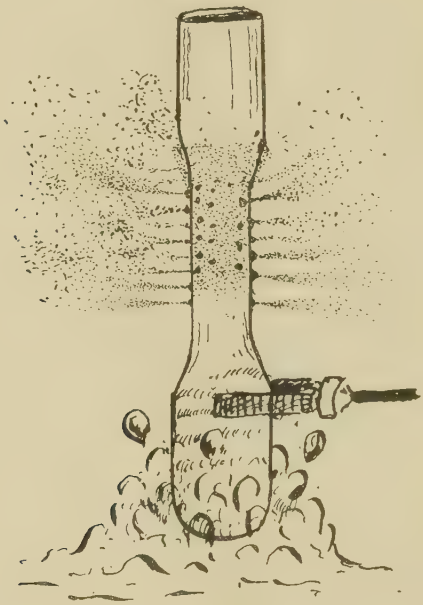
Prof. C. V. Boys has drawn my attention to the analogy between this experiment and a phenomenon produced by the

explosion of a "depth-charge." The first indication of the explosion seen at the surface is the sudden development of a great cloud of fine spray which is projected to a height of ten or fifteen feet. This is followed immediately by the rising mound of water and the great fountain, lifted by the expanding gases. The spray is due to the shock of a "pulse"-wave of almost instantaneous pressure. The spray is never seen following the explosion of a mine, which always contains a large volume of air. This acts as a cushion, and prevents the development of the instantaneous pressure.

A fog of extremely small droplets of heavy transformer oil can be formed by a collector of special construction. This is perhaps the most spectacular experiment of all. A glass tube of about 2·5 cm. diameter is closed at one end, and drawn down to a diameter of about 7 mm. at the other end. The tube is clamped to the rack and pinion stand, and the rounded bottom lowered into the oil, adjustment being made for energy density. This form of collector for compressing the radiation into small volume (if we may use this expression) is the most efficient thus far found. The constricted portion of the tube heats rapidly by internal friction, and if touched with the finger becomes unbearably hot. To distinguish between heating by internal friction and the heat developed when another body is pressed against the vibrating glass it is only necessary to operate the tube for a few seconds, shut off the power and touch the thin constricted portion with the finger. If now, with the tube adjusted for maximum heating and the oscillator working at full power, we apply a little oil with a medicine dropper to the outside of the tube above the narrowed portion, a very surprising thing happens. The oil spreads over the surface and is thrown out in jets of spray resembling smoke and a dense cloud gathers about the tube. If a match flame is brought gradually up to this cloud brilliant flashes of countless small scintillations occur resembling the sparks of the Japanese fireworks, and if the flame is brought closer, the whole cloud goes up in a grand burst of flame and the top of the tube continues to burn fiercely like a torch until the oil supply is exhausted. For some reason not quite clear the oil is unable to run down the thin portion of the tube, gathering in a ring of greater or less width at the top. If the power on the oscillator is reduced or the tube thrown out of adjustment by an up or down movement of a fraction of a millimetre the ring crawls down the tube, rising again as soon as the intensity of the vibration is increased. This driving of the oil layer up the tube is doubtless due to the fact that the energy of

the radiation travelling up the tube is greater than the energy reflected down. It is obvious that the walls of the tube are vibrating as stationary waves, since close inspection shows that the oil in the ring has gathered in more or less regularly arranged dots, and that the jets of spray shoot out from these dots (fig. 4).

Fig. 4.



A photograph of the tube in action is reproduced on Plate XIII., the clouds of spray and the jets being illuminated by sunlight and photographed under the same conditions as with the benzol fog in the beaker. Twenty or more of the small jets of spray are visible in the original photograph shooting out from the tube just below the cloud, and three vertical rows of the oil dots referred to above can be seen without difficulty between the jets.

A fog of metallic mercury was also formed with this type of collector.

With a collector of this type the amplitude of the vibration at the constricted portion frequently becomes so great that the tube is fractured in a curious manner, small irregular pieces of glass breaking away from the tube. A photograph of a tube fractured in this way is reproduced on Plate XI. fig. 8.

Flocculation of Suspended Particles in a Liquid.

In the case of particles exceeding a certain size and of a specific gravity not much greater than that of the liquid in which they are suspended, flocculation occurs the moment the liquid is traversed by the waves, the particles rushing together to form clusters which presently gather into a single dense mass just under the surface. We first noticed this effect when studying the action of the radiation on the unicellular organism paramecium, and at the moment interpreted it as a biological effect, but we presently duplicated it with fine sawdust which had soaked until waterlogged.

The phenomenon is probably the result of radiation pressure combined with shielding perhaps, or analogous to the attractions observed and studied by Bjerknes in pulsating liquids.

Effects of the waves on Chemical Reactions and Crystallization.

The effects of these high frequency radiations on Chemical reactions is under investigation by Dr. W. T. Richards of Princeton University. In work of this sort it is very necessary to distinguish between effects due to the heating of the liquid as a whole and effects due to the vibration. The liberation of dissolved gases from water has been a matter of common observation by all who have worked with super-sonics. The bubbles appear the moment the vibration is started, long before any sensible rise of temperature is observed, and instead of rising with a uniform velocity they remain suspended in the nodal planes moving up in an irregular manner, with frequent pauses. Distinct evidence has been found that certain chemical reactions are accelerated by the vibrations, the most striking case being the so-called "clock-reaction" in which the termination of the reaction is marked by the sudden change from a clear transparent solution to a deep blue one. In attempting to repeat the experiment, previously made with stearic acid, with paraffin wax, we obtained what appeared to be a crystallization of the paraffin induced by the vibration. The melted paraffin was allowed to solidify on the surface of hot water in a beaker. When the whole was quite cold, the bottom of the beaker was dipped into the vibrating oil. Small opaque white spots immediately appeared in the layer of translucent paraffin, which increased in size, forming irregular clusters. A

photograph of the sheet of paraffin (natural size) by transmitted light is reproduced on Plate XI. fig. 9. Under a Zeiss binocular stereoscopic microscope the white spots appeared to be nodules covered with protruding points which suggested a crystalline structure. They have not yet been carefully examined however. Sir W. Bragg, on seeing the photograph, remarked that paraffin crystallized in two modifications, one at the solidifying point, and another at a temperature a few degrees lower.

Dr. Richards failed to get conclusive results on the crystallization of super-saturated solutions of sodium hyposulphate by subjecting the entire amount to the vibrations, but we made one interesting experiment in which the super-sonic waves were carried to the surface of the solution by a bent glass thread. Crystallization immediately started around the tip of the thread, and also around a minute crystal which we dropped on the surface at a distance from the thread, the *type of crystallization* and *rate of growth* being different in the two cases. At the request of the Bureau of Soils, Dept. of Agriculture, we made some experiments on the dispersion of colloids from soils. In soil analysis it is often a long and tedious process to disperse the colloids adsorbed on the soil grains. It was found that the colloids of a "very difficult" soil sample sent for examination were completely dispersed into the water by a few minutes treatment to the super-sonic vibration, while by the usual methods the process of shaking violently and centrifuging has to be repeated twenty or thirty times before the colloid is completely dispersed.

Biological Effects.

Though the effects of these waves upon living matter might more properly be discussed elsewhere, it may not be out of place to mention briefly a few of the observations which we have made as they have some bearing on the physical processes involved.

In marked contrast to the flocculation, or driving together of small particles of suspended matter, which has been mentioned, we have fragmentation, or the tearing to pieces of small and fragile bodies. Filaments of living spirogyra were torn to pieces and the cells ruptured. Small unicellular organisms such as paramecium were rendered immobile by a short treatment to vibration of moderate intensity, subsequently recovering, but were killed by a longer exposure, many of them being torn open. The circumstance that all

are not treated alike is doubtless due to the fact that those which manage to keep out of the nodes of the stationary wave system are less roughly handled by the vibrations. Bacteria apparently are able to survive owing to their small size, for the fragmentation of larger bodies is due to the fact that the forces applied to their surfaces vary in magnitude and direction at different points of the body, while in the case of a bacterium the whole body is subjected to the same treatment.

Red blood corpuscles in physiological salt solution are rapidly destroyed, the turbid liquid becoming as clear as a solution of a red aniline dye.

With vibrations of less intensity the destruction is less complete, a blood count made at the end of each 15 seconds of exposure showing that the percentage destroyed decreases, a point being reached at which no further destruction occurs unless the intensity of the radiation is augmented. This means of course that some of the corpuscles, the recently formed ones perhaps, are more hardy than those of greater age. Small fish and frogs are killed by an exposure of one or two minutes, an observation also made by Langevin at Toulon with his Poulsen arc oscillator (see Plate VIII.) Mice are less sensitive, a twenty-minute exposure not resulting in death, and though at the end of the treatment the animal was barely able to move, the recovery was fairly rapid. Blood counts made with a mouse during exposure showed a diminishing number of corpuscles, until a stationary state (about 60 per cent. normal) was reached. The biologists inform us, however, that the blood count of a mouse is affected by fear, the corpuscles hiding in the liver until the danger is over! We made the count with drops taken from the tip of the tail.

We have not yet determined the cause of death in the case of the fishes and frogs. They were protected against rise of temperature as much as possible by ice fragments, dropped into the water from time to time, but this does not shield them from internal heating, which may be the cause of death, as in the case of small animals introduced into a high-frequency electric field. In the case of a mouse killed by an exposure of two minutes between the plates of an air-condenser operated at about 1000 volts with a frequency of 100 million, we found that the temperature of the body-cavity was over 113° F.

With distilled water or a fairly strong solution of salt in a test-tube between the plates of the condenser, little or no heating occurred; but for small concentrations the heating

was very marked, the maximum being for ·8 per cent., which is very nearly the amount found in mammalian blood. At lower frequencies the heating appears to be greater for distilled water, at least with high voltages. We found that one terminal of our 60,000 volt coil could be held in the fingers without the production of any sensation, but if dipped into the open end of a glass tube a metre long and filled with distilled water, caused the water to boil in less than 10 seconds. The introduction of a small amount of salt into the water, prevented the heat entirely in this case, which explains why no thermal discomfort was felt when the wire was held in the hand. The wire must be seized, however, before the current is turned on, otherwise a very vicious arc jumps to the finger producing a burn which is very slow in healing.

XXXIX. *The Electronic Theory of the Voltaic Cell.* By O. M. Corbino, *Professor of Physics in the University of Rome* *.

EVEN after the recognition on the part of physicists of the actual existence of the Volta effect as an intrinsic property of the metals, in electrochemistry one continues to identify the contact e.m.f. with that of the Peltier effect, which is so much smaller.

It is only in a recent statistical theory of the cell due to Butler †, that the Volta e.m.f. receives its due consideration for the calculation of the total e.m.f.

I propose in this paper to contribute to the clarification of this important question.

From direct experiments, as well as from the study of thermionic and photoelectric phenomena, it results at last definitely ascertained that two metals in contact give rise, also in a perfect vacuum surrounding them, to an electric field, which is, in its external effects, wholly indistinguishable from that which could be obtained by attributing to the two metals two different electrostatical potentials. This field, if the electricity is in equilibrium, must also exist in the region of contact between the two metals, by the effect of a double layer of such a strength as to compensate the different binding energy that the electrons possess relatively to the two metals. The difference of the electrostatical potentials is connected with the different extraction energies W_1 and W_2

* Communicated by the Author.

† J. A. V. Butler, Phil. Mag. xlviii. p. 927 (1924).

of the electron by two different metals. Thermodynamics teaches, in fact, that, calling V_1 and V_2 the two potentials and V their difference, the following equation must hold :

$$W_1 - W_2 = eV - eT\frac{dV}{dT},$$

where e is the electron charge and T the absolute temperature.

In this equation V is the Volta effect, while the second term represents the heat corresponding to the Peltier effect, which is, as is known, a very small part of eV. The different binding energy W of the electrons for the various metals, revealed by the thermionic and the photoelectric phenomena, thus justifies the smallness of the Peltier effect, which is considered as an unsurmountable objection against the existence of the Volta effect. Indeed, the work supplied by the quantity of electricity q in overcoming the difference of potential through the contact is mostly employed to give the electrons the necessary energy to leave a metal which attracts them more, and pass to a metal which attracts them less.

Having acknowledged the existence of the Volta effect, it is necessary to re-examine the theory of the cell, to which the difference of electrostatical potential between the electrodes and the electronic shifting which constitutes the current cannot be alien. This is what I purpose to do in the present paper.

Let us suppose that a system of two disks of different metals in electric contact be dipped in one or more electrolytical solutions, containing therefore ions of the two signs. Let it be, for instance, a Danieli cell ($Cu/CuSO_4/ZnSO_4/Zn$). Under the action of the electrical field existent between the electrodes, the anion SO_4 runs on the positive electrostatic metal, the zinc ; but, instead of neutralizing its charge and getting free, it detaches a zinc ion and remains charged in the liquid as before. At the same time the metallic cation, the copper, issues from the liquid and attaches itself to the cathode, also made of copper. The process therefore leaves unaltered the ion SO_4 and all is reduced to the detaching of one ion Zn from the zinc and upon the entrance of a ion Cu in the copper, *while in the outer circuit, through the contact of the two metals, two electrons pass from the zinc to the copper.*

It is already acknowledged, even without further details, that to a phenomenon, which manifests itself in the aforesaid manner and which can develop itself exactly in the contrary

direction opposing to the cell an outer electromotive force capable of inverting the electrostatical field in the electrolyte, the Volta electrostatical field of the electrodes in contact cannot be alien. The two copper and zinc electrodes connected externally certainly produce a field in the vacuum, and will continue to *produce it in the dielectric constituted by the solvent*; this field can be perturbed by the other eventual fields which may form themselves in the contacts of the electrolyte with the electrodes; but if, as it occurs in the Daniell cell enclosed in a short circuit, the potential difference ruling in the liquid is slightly different from that which the two electrodes would produce in the vacuum, or in the only dielectric, this means that that perturbation must not be very important. Only the concentration cells, with electrodes not different from one another, and made with the metal while in solution, can have a function independent of the Volta effect of the electrodes.

But clearer illustrations on the mechanism working in the cell and upon the importance that the existence of the Volta effect has in such a mechanism, will be supplied to us by a model of the cell which reproduces with singular correspondence all the theoretical and experimental features.

We will represent a metal with a solution, causing the dissolved body to correspond to the atom-ions of the metal and the water molecules to the electrons. Moreover, we will compare a metal dipped in a solution of one of its salts to a solution saturated in contact with the dissolved body. The inner positive ions of the metal correspond to the molecules of the dissolved body, the conduction electrons of the metal correspond to the molecules of the solvent, *i. e.* to water molecules, and lastly the electrolyte with which the metal is in contact will be represented by the dissolved body in the solid phase present in the solution. The metal may gain or lose only electrons in contact with the other metal or in the vacuum; it may gain or lose only metallic ions, *i. e.* positive ions, through the electrolyte; thus, as the solution may lose or gain only water in contact with other solutions through a semipermeable wall or the vacuum, it may lose or gain only molecules of the dissolved body in contact with the solid phase of the latter. The $Cu–CuSO_4–ZnSO_4–Zn$ combination of the Daniell cell (fig. 1) will therefore correspond to that represented in fig. 2.

In a circular tube there are two saturated solutions of two bodies, A and B, separated in π by a semipermeable fixed wall and in S by a movable piston; on both surfaces of S are collected bodies A and B in a solid state, so as to keep

the corresponding solution saturated also during the slow motion of the piston. Upon the piston S will weigh the two different osmotic pressures of the solutions, and S will move;

Fig. 1.

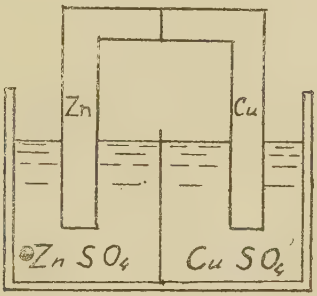
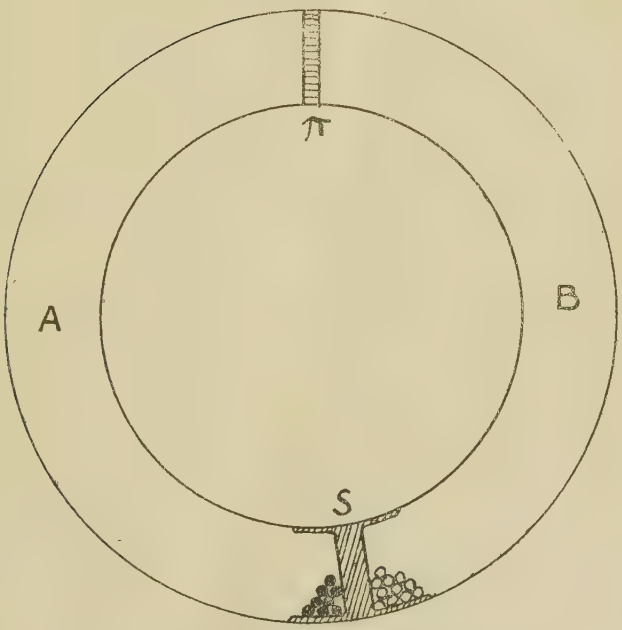


Fig. 2.



to a movement of S, for instance towards the left, will correspond a circulation of pure water across the semi-permeable wall, a diminution of volume of solution A, with a deposit of the dissolved part A, and an increase of the

volume of solution B with the dissolving of body B. The process is continuous until the piston S in its motion reaches wall π, *i. e.* until solution A disappears; of course, if a sufficient quantity of the dissolving body B is available.

A bath in which all the apparatus is dipped serves to maintain the temperature constant.

In perfect correspondence with the model, in the cell of fig. 1 the electrons circulate, outside the cell, from the zinc to the copper through the contact, which, as we have stated, acts as a semipermeable wall; at the same time, the zinc destroys itself in passing to the state of ions Zn in the liquid, while the copper from the state of ion Cu deposits itself as a metal on the copper plate, and this until there are zinc and copper sulphate available. The difference of hydrostatical pressure between A and B corresponds to the difference of the electrostatical potentials between zinc and copper.

So that the analogy with the cell may be closer, we shall suppose that, as the formation of copper from ions and electrons is a exo-energetic reaction, also the formation of the solution is so; and therefore the dissolution without osmotic work, viz. that which is studied with the calorimeter, will be esothermical in virtue of a chemical reaction between the solvent and the dissolved portion, *i. e.* water and calcium salts.

And therefore the origin of the water circulation work in the model will be the forming energy of the volume unit of the two solutions, and precisely the so-called dissolution heat with osmotic work. The portion of this formation-energy corresponding to the work production results, from the theory, as equal to the difference of the osmotic pressures of the two solutions, which, after all, is obtained also directly from the consideration of the working system of the apparatus.

Analogously for the cell will come into play the different inner potentials (photoelectrical potentials) of the two metals, and the variation of energy in the contact of the electrodes with the electrolyte, for the passage of ion Zn into solution, and for that of ion Cu on to the metal. The total available energy will be given by the formation of a certain weight of neutral copper starting from ions Cu which get in from the solution, and by two electrons which enter from the bi-metallic contact, diminished by the energy of corresponding formation of an equivalent weight of neutral zinc. Naturally these formation-energies of the metal are not to be confounded with that of the isolated atom.

The analogy can be followed further. If one opens the

tube of fig. 2 in the place of wall π, by leaving the ends free, the hydrostatical pressures balance and the water circulation stops. Thus, by detaching the two metals of the cell in the place of the electric contact, the field inside the electrolyte is annulled and the motion of the ions stops. And as the two upper and separate parts A, B of the tube might communicate through a tube containing the steam phase, which would reconstitute the circulation, thus an electronical evaporation between Zn and Cu, kept for instance in the vacuum and at a high temperature, would reconstitute the current, for also this communication is equivalent to a contact.

Further : if in the tube of fig. 2 a horizontal stoppage is made both in A and in B, above we shall have the difference of hydrostatical pressure created by the semipermeable wall, while below the liquid pressures will be almost made equal by the movable piston S. From this, one knows the essential function of the semipermeable wall, which creates and tends to maintain the difference of hydrostatic pressure, while the movable piston tends to do away with it ; hence the circulation continues on account of the contra-position of the two.

Analogously, if we cut the upper part of the bimetallic couple horizontally, above we shall have the difference of the electrostatical potential of Volta, while below, between the trunks of Zn and of Cu we shall have a difference of electrostatical potential far smaller. It can be rightly affirmed that the contact of the metals tends to maintain the difference of electrostatical potentials ; the immersion in the liquid tends to lessen it, and therefore the balance is perturbed and a continuous current is determined. This is *Volta's interpretation.*

Of course this does not exclude that the e.m.f. of the cell may be somewhat different from the Volta effect in the vacuum. The exact value of E, owing to the application of the two principles of thermodynamics, must correspond to the total variation of the free energy which occurs *in the total circuit*, according to the Gibbs-Helmholtz formula, which cannot be contrary to the synthetic interpretation given above, for it is independent of every hypothesis upon the current-production mechanism.

In connexion with the Daniell cell, for which the thermal corrective term of Helmholtz is small, the evaluation of energy $2Ee$ freed in the passage of two electrons, viz. for the shifting in the electrolyte of a bivalent metal ion, can be carried out as follows :—Let it be firstly noted that, upon

ascertaining the formation of a neutral metal where the copper deposits itself, this does not mean that neutral atoms have deposited themselves, for it is quite probable that in the metal there exist only positive ions, deprived of the valence electrons, and an inner thick cloud of conduction electrons; so that, upon constituting the neutral metal, it might well happen that the metal positive ion enters from the electrolyte and *remains as such*, viz. in the state of ion, while the electrons enter from the bimetal contact and mingle themselves in the electronic cloud. Let W^-_{Zn} be the work of photoelectrical extraction of an electron from the zinc, and W^-_{Cu} that of the copper; the cutting off of energy from the contact for the passage of two electrons from the zinc to the copper, neglecting the Peltier effect, will be $2(W^-_{Cu}-W^-_{Zn})$. In the copper-copper sulphide contact there takes place the passage of one ion Cu from the liquid to the copper, developing a quantity of free energy which we shall call W^+_{Cu}. The same may be said for the zinc, which will develop, for the passage of ion Zn in the liquid, the quantity of free energy $-W^+_{Zn}$.

We shall therefore have a total of

$$2Ee=2W^-_{Cu}+W^+_{Cu}-(2W^-_{Zn}+W^+_{Zn}). \quad . \quad . \quad (1)$$

We can thus have E, e.m f. of the cell, as a characteristic quotient of it, taken as a whole, between the electrical energy totally developed in the circuit and the quantity of electricity passed.

Let us now try to distribute E among the various contacts which have their place in the circuit. Let it be noted, in the meantime, that (1) can be put under the form:

$$E=\frac{1}{2e}(W^+_{Cu}-W^+_{Zn})+\frac{1}{e}(W^-_{Cu}-W^-_{Zn}).$$

But the last term is the Volta effect V. Therefore

$$E=V+\frac{1}{2e}(W^+_{Cu}-W^+_{Zn}). \quad . \quad . \quad . \quad . \quad (2)$$

If, as it happens in the Daniell element, the e.m.f. of the cell is very near the Volta effect between the electrodes, this means that W^+_{Cu} and W^+_{Zn} are slightly different from one another, that is to say, that the energies freed in the passage of the ion from the metal to the solution are partially compensated in the two electrodes; or even that the greatest

part of the cell work is given by the passage of the electrons from the zinc to the copper.

This result must not astonish us.

It is therefore necessary to clear a point of considerable importance. Electricity can pass from one metal to another only in the state of electrons; from a metal to an electrolyte only in the state of metal ions. But there is a property common to all the passages. At every contact where there exists on both sides a different connecting energy for electricity, there certainly exists also a difference of electrostatical potential, viz. an outer electrical field, and a double layer at the contact, equivalent to the energy difference; and *vice versâ* at every contact where between the two parts is detected a difference of electrostatical potential with an outer electrical field, there exists a difference of binding energy for electricity between the two parts themselves, and therefore, in a certain sense, a source (positive or negative) of energy for the passage of electricity through the contact. *In this sense no difference can be made between what occurs in each of the three principal contacts of the cell.*

However, if the quantities W^{+}_{Cu} and W^{+}_{Zn} (variations of free energy for the passage of an ion from the metal to the liquid) are different from zero, there will most likely exist a difference of potential between a metal and liquid and an outer electrical field between them; and besides, as there certainly exists the difference of electrostatical potential between the two metals upon coming into contact, viz. the outer electrical field, there will undoubtedly exist in the contact a metal-electronic seat of energy variations for the passage of electrons from one metal to another.

The only difference between the three contacts is the different kind of electrical ion which can get across them—*i. e.* the electron for the bimetallic contact, the metallic ion for the contact with the electrolytes; but all of them contribute to the production of current with the corresponding variations of energy and the double layers which arise from them. Therefore it is not at all justifiable to neglect the first and to look at the other two only. *The current arises from the fact that the algebraic sum of the strengths of the three double layers is not zero.*

Considering the formula (1), we have stated that E being near V, it results that W^{+}_{Cu} and W^{+}_{Zn} are near each other; but each of them might either be very large or very small. To W^{+}_{Cu} and W^{+}_{Zn} correspond the differences of metal-liquid

potentials, considered in Nernst's formula, and that they can, as he puts it, depend on the concentration of the metal ions in the solution. They should, however, be measured *electrostatically*, and not by the usual means of electrochemistry, which *purposely neglects the differences of electrostatic potential in the contacts of metals*, and is always subjected to the uncertainty of the so-called zero-point of the absolute electrolytical potentials.

So it is customary to attribute to the absolute potential of the normal calomel electrode the value $-0{\cdot}560$ volt; then the normal potentials P_M of the various metals are known from the Wilsmore or Potential-Commission Tables; they can be referred to the same zero-point, in respect to which the normal electrode has the absolute potential $-0{\cdot}560$. Therefore the cell formed by metal M, by a salt of its own, in normal solution, and by the normal electrode, has the e.m.f.

$$E = P_M + 0{\cdot}560,$$

which is independent of the choice of the zero-point.

But for the formula (2), if $-0{\cdot}560$ is the true absolute potential of the normal electrode, the following equation must hold:

$$E = M/Hg - \frac{1}{ne} W_M^+ + 0{\cdot}560,$$

where M/Hg is the Volta effect between the metal and Hg, and n is the valence of the ions M^+.

We thus obtain as potential difference V_M^+ between the metal and liquid:

$$V_M^+ = \frac{1}{ne} W_M^+ - M/Hg - P_M.$$

And therefore, in the hypotheses made, in order to have the e.m.f. in the metal-electrolyte contact, we must subtract P_M from the Volta effect M/Hg.

The knowledge of the electrostatical potential difference between Cu and $CuSO_4$ would give the exact value of W_{Cu}^+ and the same for the zinc.

And then, having from the photoelectrical data also W_{Cu}^-, W_{Zn}^-, one might reconstitute the total formation-work or the | metal-ions, electrons | mixture which constitutes the neutral metal. These data would be of remarkable interest: they would supply, by the difference between copper and zinc, the e.m.f. of the Daniell cell.

In the ordinary theory of the Daniell cell, we get the right value of the e.m.f., considering, instead of the formation energies of the metals, the variation of energy for the formation of zinc sulphate and the decomposition of copper sulphate ; and therefore the difference of the corresponding heats of formation (Zn, O, SO_3, water), (Cu, O, CuO_3, water), as determined by Thomsen.

But in this way we introduce elements wholly extraneous to the true functioning of the cell, which is practically independent of the presence of the acid anion SO_4. Of course these extraneous elements are eliminated by subtracting the two heats of formation.

If the cell contains any other salts instead of sulphates, we must calculate the e.m.f. by means of other thermochemical experiments, still obtaining, by Hess's rule, the same value for the formation-heats of the dissolved homologous salts of Cu and Zn.

With considerably greater simplicity the electronic theory takes into account the formation-energies of the electrodes, which do not depend upon the acid anion, but only, and to a small extent, upon the concentration of the metallic ions in the solution.

In Nernst's theory we find the same simplification and unification of the cells having the same electrodes : indeed, only the dissolution pressure of the metal and the osmotic pressure of the metallic ions in the solution come into account, and not the presence of the acid anion.

They are thus four quantities which characterize the working of the cell : the ionic contribution W^+_{Cu} and the electronic contribution $2W^-_{Cu}$ relative to the copper, and the two analogous elements relative to the zinc. The part $2(W^-_{Cu} - W^-_{Zn}) = 2eV$, where V is the Volta effect, can be supplied only by the electronic efflux, and the remainder by the electrolyte ; and therefore, V being very near E, the greater part of the work obtained is due to the absorption of electrons, which the copper accomplishes from the zinc, viz. to the same cause as the Volta effect, while the displacement-works of the metal ions are mostly compensated.

Conclusion.

Having ascertained the existence of the Volta effect also in the vacuum, and therefore independently of any chemical action, the bimetal couple, *i.e.* copper zinc, forms a natural and perpetual means acting to produce in a space

even of large dimensions an electrostatical field ; thus, like a permanent magnet, it forms (with less stability, however) around itself a magnetic field. The origin of the energy of this electrostatical field is simply physical : it arises from the different binding energies of the conduction electrons to the various metals.

In the cell which is obtained by dipping a bimetal couple into a ionized gas, the electrostatical field due to the Volta effect produces a permanent current without supplying an energy of its own, but in so far as there exists an outer source of energy which ionizes the gas. In this case the electrostatical field simply causes, without doing any work, a directing control of the ionic motion, and therefore a current in the wire which connects the two disks ; the energy is that of the recombination of the ions. But the field cannot be neglected or ignored. Even in a permanent Pacinotti magnet-dynamo the current is produced by means of the outer mechanical work, but the inductive field is an indispensable condition in order that work may become electrical power.

In hydro-electrical cells the task of the Volta effect is far more important ; thus in the Daniell cell the current is produced by means of the formation of neutral copper and the destruction of neutral zinc, and, as has already been seen, in this process one must hold that most of the work obtained is due to the electronic passage, and most of the e.m.f. is upon the contact of the two different metals.

But one might get the extreme case of a cell where the electronic displacement alone can produce electrical current and mechanical work. It will suffice to think of two neutral copper and zinc disks with a large surface, placed at a distance and connected by means of a wire. On account of their approach, there will be produced a current and mechanical work due to the fact that some of the electrons leave the zinc disk to go towards the copper one, which attracts them more strongly. The smallness of the electrostatical capacity prevents the afflux possibility from becoming a great number of electrons ; but if, on a block of copper, electrons are caused to run up together on one side, and positive ions on the other, so as to leave the electrostatical potential unchanged, the currents and energies obtained can become much greater. It is this, which, after all, occurs in the hydro-electrical cell. This is why the explanation of the working of the cell on the basis of the Volta effect cannot lead to substantial contradictions, and must, on the contrary, be considered as scientifically correct.

XLI. *The Molecular Scattering of Light in a Binary Liquid-Mixture.* *By* Prof. C. V. Raman, *F.R.S.**

IN the Philosophical Magazine for March 1927 appears a note under this title by Dr. K. C. Kar, purporting to be a criticism of the theory of light-scattering† in liquid-mixtures developed some years ago by the present writer with Dr. Ramanathan. An examination of the note shows it to be based entirely on a misconception.

In his classical paper on critical opalescence, A. Einstein ‡ discussed the scattering of light in liquid-mixtures, considering, however, only the optical effect due to the local fluctuations of composition occurring in the mixture. The object of the paper by the present writer with Dr. Ramanathan in the Philosophical Magazine for January 1923 was, in the first place, to emphasize that the local fluctuations of density in the mixture have also to be taken into account, and in the second place, to show how by considering these two effects together with the influence of the optical anisotropy of the molecules, the observed facts of light-scattering in mixtures may be explained. The formulæ necessary for our purpose were deduced in a perfectly simple and straightforward fashion, in terms of experimentally measurable quantities, from the well-known relation between entropy and thermodynamical probability. It was shown that they furnished a satisfactory explanation of the remarkable changes in the intensity and polarization of the scattered light which occur when the composition of the mixture and its temperature are varied. Subsequent experimental work in the field has fully supported our conclusions §. R. Gans ‖, who followed us, quotes our formulæ with approval, and indeed has checked their correctness by following a method of derivation differing in detail from ours. He also points out ¶, as is indeed quite obvious, that the expression for the fluctuations of composition is obtained in the form given by Einstein only when the specific volume of the mixture is neglected in comparison with that of the vapour. The same result is also clearly seen in our paper, as also in the earlier work of Zernike **. The correction involved is, however, usually quite negligible.

We hardly think that any reader of our paper of 1923 would have found a difficulty in following our arguments or

* Communicated by the Author.

† C. V. Raman and K. R. Ramanthan, Phil. Mag. xlv. p. 213 (1923).

‡ A. Einstein, *Ann. d. Physik*, xxxiii. p. 1275 (1910).

§ See, for instance, J. C. K. Rav, Phys. Rev. xxii. p. 78 (1923).

‖ R. Gans, *Zeit. f. Physik*, xvii. p. 353 (1923).

¶ R. Gans, 'Contribucion estudio de las ciencias, La Plata,' vol. iii. (footnote on page 290, 1923).

** F. Zernike, Doctorate Thesis, Amsterdam (1914).

checking the correctness of the formulæ deduced. Dr. Kar, however, appears to have set out with a fixed idea that there must be some error in our work, and in trying to unearth it falls into various errors himself. Most of his troubles arise from his having failed to notice that the mechanism of the process we follow in our paper is different from that of Einstein, and indeed is somewhat simpler. Whereas Einstein finds merely the work necessary to change the concentration of the mixture by an infinitesimal amount from one value to another, both differing from that of the bulk of the mixture, we, on the other hand, evaluate directly the total work necessary to change the concentration of a small volume of the mixture from its normal (mean) value to one slightly different. For this purpose a volume $m_1\Delta k v_2$ of the vapour of the second component is withdrawn from the main reservoir, and is then pushed into the smaller reservoir, which has *initially* the same concentration, the latter being altered as the result of the process. The whole volume pushed in is $m_1\Delta k v_2$, and the partial pressure in the smaller reservoir is initially p_2, and rises spontaneously and gradually to $p_2+\Delta p_2$ at the end of the process. The work done in the process is obviously equal to the total volume pushed in, multiplied by the mean of the initial and final pressures. It is not necessary, as Dr. Kar seems to imagine, to compress the vapour initially to a higher pressure. Indeed, if this were done, the process would not be reversible.

When the error indicated above in Dr. Kar's work is set right, there is little in his communication left to comment upon. He refers in his note to a paper by him published in the *Physikalische Zeitschrift*. In view of the fact, however, that this and other writings of his on light-scattering have already been subjected to criticism by Fürth*, by Ornstein and Zernicke†, and by Mitra ‡, it would appear that no useful purpose would be served by discussing them further in the pages of the Philosophical Magazine.

210 Bowbazar Street, Calcutta,
31st March, 1927.

Note added in proof, dated 27th July, 1927.—In a paper appearing in the 'Indian Journal of Physics,' vol. ii., the present writer has discussed the relation between light-scattering and osmotic pressure in solutions. The formulæ obtained are in complete agreement with those given in the Philosophical Magazine for January 1923, when the known relation between osmotic pressure and vapour tension is kept in view.

* R. Fürth, *Phys. Zeit.* xxv. p. 111 (1924).
† L. S. Ornstein and F. Zernike, *Phys. Zeit.* xxvii. p. 761 (1926).
‡ M. N. Mitra, Ind. Journ. Phys. i. p. 137 (1926).

XLI. *Note on Green's Lemma and Stokes's Theorem.* By A. J. Carr, *M.A., Lecturer in Mathematics, Bradford Technical College* *.

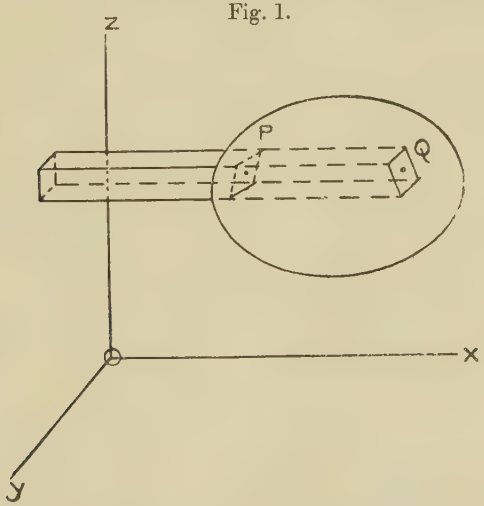
§ 1. My attention was recently drawn to weak points in the usual proof of Green's Lemma as employed in at least seven treatises on various branches of Applied Mathematics; quite as many have also faulty proofs of Stokes's Theorem. The object of this paper is to expose and also to correct these discrepancies.

I shall deal first with the well-known Green's Lemma, viz.,

$$\iiint_{V_0}\left(\frac{\partial U}{\partial x}+\frac{\partial V}{\partial y}+\frac{\partial W}{\partial z}\right)dx\,dy\,dz=\iint_S(lU+mV+nW)dS.$$

Except in treatises on Analysis, this is always proved by taking a figure such as that in the diagram and stating that

Fig. 1.



$$\begin{aligned}&\iiint\frac{\partial U}{\partial x}dx\,dy\,dz\\&=\iint(U_Q-U_P)\,dy\,dz\\&=\iint[U_Q l_Q dS_Q-U_P(-l_P)dS_P]\\&=\iint U l dS,\end{aligned}$$

taken over the whole bounding surface.

* Communicated by the Author.

This is undoubtedly true. In fact,

$$\iiint\left(\frac{\partial U}{\partial x}+\frac{\partial V}{\partial y}+\frac{\partial W}{\partial z}\right)dx\,dy\,dz$$

$$=\iiint\frac{\partial U}{\partial x}\,dx\,dy\,dz+\iiint\frac{\partial V}{\partial y}\,dx\,dy\,dz+\iiint\frac{\partial W}{\partial z}\,dx\,dy\,dz$$

$$=\iint_S U l\,dS_1+\iint_S V m\,dS_2+\iint_S W n\,dS_3.$$

But these integrals can *not* be grouped together and written as

$$\iint_S (lU+mV+nW)\,dS\ ;$$

for dS_1 is the section made at (x, y, z) on S by a prism $dy\,dz$ parallel to Ox, dS_2 that made by $dz\,dx$ parallel to Oy, dS_3 by $dx\,dy$ parallel to Oz. These are three different elementary areas, for in general it is not possible to subdivide a surface S in such a way that dS always, or indeed ever, projects into $dy\,dz$, $dz\,dx$, $dx\,dy$, on the three co-ordinate planes, so that we cannot say, "Similarly for $\iiint(\partial V/\partial y)\,dx\,dy\,dz$, $\iiint(\partial W/\partial z)\,dx\,dy\,dz$. Hence etc." (*v.* § 4 *post.*).

§ 2. Green's Lemma is of course true, but the proof should be handled so that the surface is only subdivided in *one* way. To do this we notice that if

$$x=f_1(u, v, w),\quad y=f_2(u, v, w),\quad z=f_3(u, v, w)\ .\quad (1)$$

where (u, v, w) is any other system of co-ordinates, then a surface whose equation is (say)

$$F(x, y, z)=0\ .\ .\ .\ .\ .\ .\ .\quad (2)$$

establishes between u, v, w such a relation as

$$w=\phi_1(u, v),\quad .\ .\ .\ .\ .\ .\ .\quad (3)$$

and on substituting in x, y, z, we find

$$x=\psi_1(u, v),\quad y=\psi_2(u, v),\quad z=\psi_3(u, v).\quad .\quad (4)$$

These new equations can therefore replace (2).

Moreover, if another surface

$$F_1(x, y, z)=0\ .\ .\ .\ .\ .\ .\ .\quad (5)$$

or

$$w=\phi_2(u, v)\ .\ .\ .\ .\quad (6)$$

intersect (2) in some curve, the equation of this curve can be put as

$$w=\phi_1(u, v)=\phi_2(u, v),$$

i. e.
$$v=\lambda(u)$$

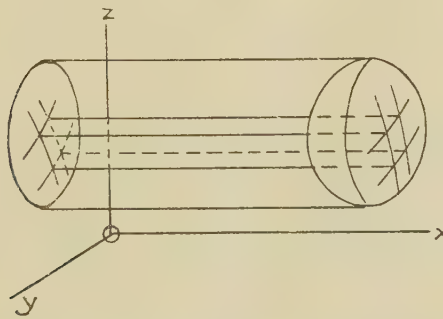
or
$$u=g(\theta), \quad v=h(\theta);$$

whence

$$x=\xi(\theta), \quad y=\eta(\theta), \quad z=\zeta(\theta).$$

As u, v can be represented in a plane, the surface (2) bounded by the curve in which it is cut by (5) is transformed into a region of the (u, v) plane bounded by the corresponding curve. The parallels to $O'u$, $O'v$ respectively are transformed into the curves on $F=0$, in which this surface is cut by the surfaces $u=$const., $v=$const., and this is the single method of subdivision which should replace the three independent ones usually adopted for Green's Lemma. These curves project

Fig. 2.



into curves $u=$const., $v=$const. on the yz plane, upon which

$$y=\psi_2(u, v), \qquad z=\psi_3(u, v),$$

the bounding curve C_1 being the projection of C, the locus of the points at which parallels to Ox touch the surface. This latter may be supposed the curve above referred to as the intersection of F, F_1.

The superficial area dS between

$$u=\alpha, \quad u=\alpha+d\alpha, \quad v=\beta, \quad v=\beta+d\beta,$$

projects into $l d\mathrm{S}=d\alpha d\beta \,.\, \partial(y, z)/\partial(\alpha, \beta)$, and here we *can* use "similarly" and say that dS projects on the zx and xy planes respectively into $m d\mathrm{S}=d\alpha d\beta \,.\, \partial(z, x)/\partial(\alpha, \beta)$, $n d\mathrm{S}=d\alpha d\beta \,.\, \partial(x, y)/\partial(\alpha, \beta)$. If on the yz plane we apply

the intermediate transformation (y', z'), where

$$y'=u, \quad z'=z=\psi_3(u, v)=\psi_3(y', v),$$

so that $$v=\pi(y', z')$$

or $$y=\psi_2(y', v)=\pi_1(y', z'), \quad z=z' ;$$

then
$$\begin{aligned} l d\mathrm{S} &= du\,dv\,.\,\partial(y, z)/\partial(u, v) \\ &= du\,dv\,.\,\frac{\partial(y, z)}{\partial(y', z')}\,.\,\frac{\partial(y', z')}{\partial(u, v)} \\ &= du\,\frac{\partial \pi_1(y', z')}{\partial y'}\,.\,\frac{\partial \psi_3(u, v)}{\partial v}\,dv \\ &= du\,\frac{\partial y}{\partial u}\,.\,\frac{\partial z}{\partial v}\,dv \\ &= dy_u dz_v. \end{aligned}$$

This, of course, is really equivalent to writing

$$z=\psi_3(u, v), \quad \text{i. e.} \quad v=\pi(u, z), \quad y=\psi_2(u, v)=\pi_1(u, z);$$

whence
$$\partial(y, z)/\partial(u, v)=\partial y/\partial u\,.\,\partial z/\partial v,$$

since y, z are independent variables inside S_1, the region on the yz plane bounded by the closed contour C_1.

Similarly $m d\mathrm{S}=dz_u dx_v$, $n d\mathrm{S}=dx_u dy_v$, equivalent to what Applied Mathematical writers usually express as $l d\mathrm{S}=dx\,dy$, $m d\mathrm{S}=dy\,dz$, $n d\mathrm{S}=dz\,dx$. But notwithstanding that these last three equations can never be made wholly consistent, we can none the less prove that $\iint_{\mathrm{S}_1} \mu\,dy\,dz$ is equal to $\iint_{\mathrm{S}_1} \mu\,d\sigma_1$, where

$$d\sigma_1=du\,dv\,.\,\partial(y, z)/\partial(u, v) \neq dy\,dz,$$

for both these integrals are equal to the volume of the cylinder whose "upper" surface is given by $x=\mu(y, z)$, and whose section on the yz plane has been subdivided in two different ways, firstly by parallels to Oy, Oz, secondly by the two systems of curves u, v.

Hence results which are true for the limiting case of an aggregate of elements are not necessarily true for the finite individual elements, however small these be.

§ 3. All this discussion leads to

$$\begin{aligned} \mathrm{I}_1 &= \iiint_{\mathrm{V}_0} \partial \mathrm{U}/\partial x\,.\,dx\,dy\,dz = \iint dy\,dz \int_{x_1}^{x_2} \partial \mathrm{U}/\partial x\,.\,dx \\ &= \iint [\mathrm{U}(x_2, y, z)-\mathrm{U}(x_1, y, z)]\,dx\,dy, \end{aligned}$$

where $x_2=\mu_2(y, z)$, $x_1=\mu_1(y, z)$ are the equations to the

"upper" and "lower" parts of S. That is,

$$I_1 = \iint_S U dy\,dz \text{ extended over the whole exterior surface,}$$

$$= \iint_{S_1} U[\mu(y, z), y, z] d\sigma_1$$

$$= \iint_{S_1} U \partial(y, z)/\partial(u, v) \,.\, du\,dv$$

$$= \iint_S U l\, dS;$$

and

$$I = \iiint_{V_0} (\partial U/\partial x + \partial V/\partial y + \partial W/\partial z)\, dx\,dy\,dz$$

$$= I_1 + I_2 + I_3$$

$$= \iint U l\, dS + \iint V m\, dS + \iint W n\, dS$$

$$= \iint_S (lU + mV + nW)\, dS,$$

where dS *is now the same in each integral.*

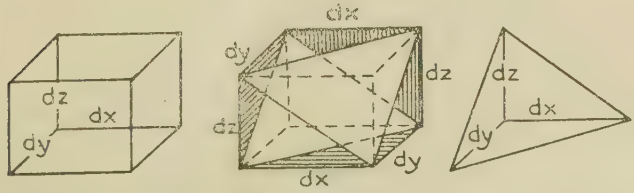
This method of subdivision would appear to point to the existence in space of n dimensions of the analogue to Green's Lemma for an n-tuple and an $(n-1)$-tuple integral, viz.,

$$\int\int \ldots \int \sum_{r=1}^{n} \partial U_r/\partial x_r \,.\, dx_1 dx_2 \ldots dx_n$$

$$= \int\int \ldots \int \sum_{r=1}^{n} (-)^{n-r} U_r \frac{\partial(x_1, \ldots x_{r-1}, x_{r+1}, \ldots x_n)}{\partial(u_1, \ldots\ldots\ldots\ldots u_{n-1})} du_1 du_2 \ldots du_{n-1}.$$

§ 4. Again, Stokes's very important theorem is frequently proved by supposing it possible to divide up a surface into elements, each of which projects into rectangles $dy\,dz$, $dz\,dx$, $dx\,dy$ on the three co-ordinate planes. It is easy to see, however, from an elementary parallelepiped that no such surface can exist. True, a *triangle* can project into triangles of areas $dy\,dz/2$, $dz\,dx/2$, $dx\,dy/2$, but no surface other than a plane can be subdivided into such a set of contiguous triangles, all of which satisfy this condition.

Fig. 3.



However, by striating the surface by the u, v curves we can obtain results which will apply directly to n dimensions,

if we suppose a "diaphragm" given by the variables u, v such that

$$x_r = f_r(u, v) \qquad (r = 1, 2, \ldots n)$$

and bounded by a closed "contour" C, for which

$$u = \phi_1(\theta), \quad v = \phi_2(\theta).$$

The diaphragm and its bounding contour then transform into a region A of the (uv) *plane* bounded by a plane curve γ, and

$$\begin{aligned} J_n &= \int_C \Sigma X \, dx \\ &= \int_\gamma \left\{ \left(\sum_{r=1}^{n} X_r \frac{\partial x_r}{\partial u} \right) du + \left(\sum_{r=1}^{n} X_r \frac{\partial x_r}{\partial v} \right) dv \right\} \\ &= \iint_A \left\{ \frac{\partial}{\partial u} \left(\sum_{r=1}^{n} X_r \frac{\partial x_r}{\partial v} \right) - \frac{\partial}{\partial v} \left(\sum_{r=1}^{n} X_r \frac{\partial x_r}{\partial u} \right) \right\} du \, dv, \end{aligned}$$

applying "Green's Theorem" in two dimensions*. That is,

$$\begin{aligned} J_n &= \iint_A \sum_{r=1}^{n} \left(\frac{\partial X_r}{\partial u} \frac{\partial x_r}{\partial v} - \frac{\partial X_r}{\partial v} \frac{\partial x_r}{\partial u} \right) du \, dv \\ &= \iint_A [v, u] \, du \, dv, \end{aligned}$$

where $[v, u]$ is the Lagrange bracket-expression for the set of variables (x_r, X_r). The formula may be left in this shape, but is preferably extended to

$$\begin{aligned} J_n &= \iint_A \sum_{r=1}^{n} \left(\frac{\partial x_r}{\partial v} \sum_{s=1}^{n} \frac{\partial X_r}{\partial x_s} \frac{\partial x_s}{\partial u} - \frac{\partial x_r}{\partial u} \sum_{s=1}^{n} \frac{\partial X_r}{\partial x_s} \frac{\partial x_s}{\partial v} \right) du \, dv, \\ &= \iint_A \sum_{r=1}^{n} \sum_{s=1}^{n} \frac{\partial X}{\partial x_s} \frac{\partial (x_s, x_r)}{\partial (u, v)} \, du \, dv, \end{aligned}$$

or again,

$$= \iint_A \sum_{r,s}^{n} \left(\frac{\partial X_s}{\partial x_r} - \frac{\partial X_r}{\partial x_s} \right) \frac{\partial (x_r, x_s)}{\partial (u, v)} \, du \, dv,$$

the summation being extended over all pairs of the variables.

Putting $x_1 = x$, $x_2 = y$, $x_3 = z$; $X_1 = X$, $X_2 = Y$, $X_3 = Z$, the special case of three dimensions yields at once the original

* Goursat, 'Mathematical Analysis' (Hedrick's transl. 1904), § 126.

Stokes's theorem, viz.,

$$\begin{aligned}
\mathrm{J}_3 &= \int_{\mathrm{C}} \left(\mathrm{X}\frac{dx}{ds} + \mathrm{Y}\frac{dy}{ds} + \mathrm{Z}\frac{dz}{ds} \right) ds \\
&= \iint_{\mathrm{A}} \left\{ \left(\frac{\partial \mathrm{Z}}{\partial y} - \frac{\partial \mathrm{Y}}{\partial z} \right) \frac{\partial(y, z)}{\partial(u, v)} + \left(\frac{\partial \mathrm{X}}{\partial z} - \frac{\partial \mathrm{Z}}{\partial x} \right) \frac{\partial(z, x)}{\partial(u, v)} \right. \\
&\qquad \left. + \left(\frac{\partial \mathrm{Y}}{\partial x} - \frac{\partial \mathrm{X}}{\partial y} \right) \frac{\partial(x, y)}{\partial(u, v)} \right\} du\, dv \\
&= \iint_{\mathrm{S}} \left\{ l \left(\frac{\partial \mathrm{Z}}{\partial y} - \frac{\partial \mathrm{Y}}{\partial z} \right) + m \left(\frac{\partial \mathrm{X}}{\partial z} - \frac{\partial \mathrm{Z}}{\partial x} \right) \right. \\
&\qquad \left. + n \left(\frac{\partial \mathrm{Y}}{\partial x} - \frac{\partial \mathrm{X}}{\partial y} \right) \right\} d\mathrm{S} \qquad (v.\ \S\ 2).
\end{aligned}$$

J_3 may also be exhibited as the sum of three *separate* integrals,

$$\begin{aligned}
\mathrm{J}_3 &= \iint \left(\frac{\partial \mathrm{Z}}{\partial y} - \frac{\partial \mathrm{Y}}{\partial z} \right) dy\, dz + \iint \left(\frac{\partial \mathrm{X}}{\partial z} - \frac{\partial \mathrm{Z}}{\partial x} \right) dz dx \\
&\qquad + \iint \left(\frac{\partial \mathrm{Y}}{\partial x} - \frac{\partial \mathrm{X}}{\partial y} \right) dx\, dy.
\end{aligned}$$

It is not, however, legitimate to group them under one integral sign, since this implies that dx, dy, dz are taken at the point (x, y, z), thus forming on the surface an elementary parallelepiped which can in nowise be transformed into an element of surface.

In fact, generally,

$$\mathrm{J}_n = \sum_{r,s}^{n} \iint \left(\frac{\partial \mathrm{X}_s}{\partial x_r} - \frac{\partial \mathrm{X}_r}{\partial x_s} \right) dx_r dx_s.$$

§ 5. Since writing the foregoing, I have been reminded that Clerk Maxwell uses a somewhat similar proof * ; but on examining his proof, it does not seem to me quite so general as the one given above. For instance, one of his α (or u) curves must coincide with the contour S. But we have seen that this is not at all necessary, it being more convenient to notice that on this contour a relation exists between u, v which transforms it into a plane closed curve on the uv plane. Besides, Maxwell's proof does not draw out the essential fact that Stokes's Theorem is but Green's Theorem in two dimensions for a skew curve bounding a non-planar surface. Goursat † does use this, but his method

* 'Electricity and Magnetism,' vol. i. § 24.

† *Loc. cit.* § 136.

applies only to three dimensions, depending as it does, essentially on the direction-cosines of the normal at a point of the surface and not showing that Stokes's Theorem is reduced to Green's Theorem *entirely* by a transformation to any uv plane.

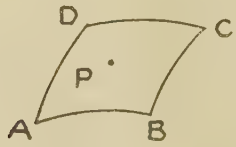
The importance of the n-dimensional form of Stokes's Theorem is seen in such problems as the dynamical one involving the reduction of the relative integral-invariant $\int\Sigma p\,dq$ to the absolute integral-invariant $\iint[\lambda, \mu]d\mu\,d\lambda$, where μ, λ do not vary with the time t, but are characteristic solely of the trajectory on which lies the point $(q_1, q_2, \ldots q_n)$, the sufficient condition for the reduction being the existence of a function $\mathrm{H}(q_1, q_2, \ldots q_n, p_1, p_2, \ldots p_n, t)$, such that

$$dq_r/dt = \partial\mathrm{H}/\partial p_r, \quad dp_r/dt = -\partial\mathrm{H}/\partial q_r\ ^*.$$

Here is implied the $\mu\lambda$ (or uv) transformation, but no proof is given. Indeed, I have not before seen a proof depending on such a transformation. Most proofs in Applied Mathematical treatises rely on striating a surface and then taking three points respectively inside the projections (supposed $dy\,dz$, $dz\,dx$, $dx\,dy$) of a typical cell whose area is $d\mathrm{S}$.

§ 6. This method, which uses no transformation, can quite adequately and far less erroneously be analysed by taking a point inside the cell itself instead of in its projections, the striating curves being, as before, $u=$const., $v=$const.

Fig. 4.



For take $\mathrm{P}(u=\alpha,\ v=\beta)$ at the centre of a typical cell ABCD, where, on AB, $v=\beta-d\beta/2$, and on BC, $u=\alpha+d\alpha/2$, while on CD, $v=\beta+d\beta/2$, DA being $u=\alpha-d\alpha/2$; also, for brevity, let $f^{(u)}=\partial f(u, v)/\partial u$, etc. Then, since always,

$$\int\Sigma \mathrm{X}\,dx = \int\Sigma[\mathrm{X}\,.\,x^{(u)}du + \mathrm{X}\,.\,x^{(v)}dv]$$
$$= \int[\mathrm{F}_1(u, v)\,du + \mathrm{F}_2(u, v)\,dv] \quad \text{(say)},$$

* Whittaker, 'Analytical Dynamics,' § 136.

we have

$$\int_{AB} \sum_1^n X_r dx_r = \int_{\alpha-d\alpha/2}^{\alpha+d\alpha/2} F_1(u, \beta - d\beta/2)\, du$$

$$= \int_{\alpha-d\alpha/2}^{\alpha+d\alpha/2} [F_1(\alpha, \beta) + (u-\alpha)F_1^{(\alpha)}(\alpha, \beta) - (d\beta/2) \,.\, F_1^{(\beta)}(\alpha, \beta)]\, du.$$

So

$$\int_{CD} \sum_1^n X_r dx_r = \int_{\alpha+d\alpha/2}^{\alpha-d\alpha/2} F_1(u, \beta + d\beta/2)\, du$$

$$= -\int_{\alpha-d\alpha/2}^{\alpha+d\alpha/2} [F_1(\alpha, \beta) + (u-\alpha)F_1^{(\alpha)}(\alpha, \beta) + (d\beta/2) \,.\, F_1^{(\beta)}(\alpha, \beta)]\, du.$$

Hence

$$\int_{AB} + \int_{CD} = -d\beta \int_{\alpha-d\alpha/2}^{\alpha+d\alpha/2} F_1^{(\beta)}(\alpha, \beta)\, du$$

$$= -d\beta \,.\, F_1^{(\beta)}(\alpha, \beta)\, d\alpha.$$

Thus

$$\int_{BC} + \int_{DA} = +d\alpha \,.\, F_2^{(\alpha)}(\alpha, \beta)\, d\beta.$$

Adding,

$$\int_{ABCDA} \Sigma X\, dx = [F_2^{(\alpha)}(\alpha, \beta) - F_1^{(\beta)}(\alpha, \beta)]\, d\alpha\, d\beta$$

$$= \sum_1^n \left\{ \frac{\partial}{\partial \alpha} [X_r \,.\, x_r^{(\beta)}] - \frac{\partial}{\partial \beta} [X_r \,.\, x_r^{(\alpha)}] \right\} d\alpha\, d\beta$$

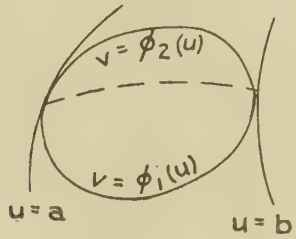
$$= \sum_1^n \left\{ \frac{\partial X_r}{\partial \alpha} \frac{\partial x_r}{\partial \beta} - \frac{\partial X_r}{\partial \beta} \frac{\partial x_r}{\partial \alpha} \right\} d\alpha\, d\beta$$

$$= [\beta, \alpha] d\alpha\, d\beta = f(\alpha, \beta)\, d\alpha\, d\beta \quad \text{(say)}.$$

From this point onward the proof proceeds on exactly the same lines as the transformation one. This method, however, seems to me unsatisfactory for an *Applied* Mathematics book, for it entails rigorous discussions of the integrals round irregular partitions at the contour itself, and for n dimensions we cannot determine, except in imagination by analogy with three dimensions, what sort of thing a contour may be,—and in any case such discussion is interesting largely to pure mathematicians, who will find the proof for three dimensions

in Goursat, *loc. cit.* § 124. For if we take $u=a$, $u=b$ to be the bounding curves and let the "lower" and "upper" portions of the contour have equations $v=\phi_1(u)$, $v=\phi_2(u)$

Fig. 5.



respectively, then we only need to put u for x, v for y, and Goursat's discussion of the double integral

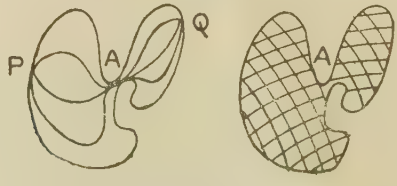
$$\int_a^b dx \int_{y=\phi_1(x)}^{y=\phi_2(x)} f(x, y)\, dy$$

holds word for word for our integral, viz.,

$$\int_a^b du \int_{v=\phi_1(u)}^{v=\phi_2(u)} f(u, v)\, dv.$$

The same writer's proof of Stokes's Theorem has already been referred to. That it is three dimensional only is a charge which can also be levelled against that of Jeans * and O. W. Richardson †. Their proof somewhat resembles my second one above, if we write d for $du\,.\,\partial/\partial u$ and δ for $dv\,.\,\partial/\partial v$, so that $\partial(y, z)/\partial(u, v)\,.\,du\,dv$ becomes $(dy\,\delta z - dz\,\delta y)$. Their method, viz. of varying the path of integration from P to Q, would hardly seem to hold good for a curve such as

Fig. 6.



that shown; the various paths would become terribly congested at A. The uv striation method, however, is obviously still sound.

* Math. Theory of Elec. § 439 (3rd ed).

† 'Electron Theory of Matter,' pp. 91–94 (1916).

Summary.

(1) The usual proofs for Green's Lemma and Stokes's Theorem to be found in most Applied Mathematical books are incorrect in that they assume it possible to subdivide a curved surface into elements, each of which has the three projections $dy\,dz$, $dz\,dx$, $dx\,dy$. No such element (and, *a fortiori*, surface) can even be realized.

(2) It is easy to substitute a proof which depends on a single change of variables (x, y, z) to (u, v), thereby transforming a curved surface into a plane one and its skew contour into a plane curve. To the new plane region we apply the two-dimensional form of Green's Theorem.

(3) Alternatively, we can attack Stokes's Theorem directly (as is usually done in text-books), without reference to a plane region.

(4) For Stokes's Theorem, either of these two methods can be extended to n dimensions, a fact which does not hold with respect to any of the proofs I have so far seen. In particular, Eddington * proves Stokes's Theorem for four dimensions as a *tensor* equation. Here, however, no such limitation is imposed.

XLII. *Light-Quanta and Maxwell's Equations.* *By* N. Rashevsky †.

In a recent interesting paper, published in this Magazine, Prof. N. P. Kasterin ‡ made an attempt to show that, in spite of the generally accepted opinion, the conception of light corpuscles is compatible with Maxwell's equations and that the form of the light-quantum theory which has been proposed by Sir J. J. Thomson § may be obtained as a particular solution of Maxwell's equations, provided we also consider discontinuous solutions of these equations.

The whole question having an importance of principle, t may be of interest to discuss here somewhat at length some of the difficulties to which Prof. Kasterin's solution leads. It should, however, be emphasized at once that it is not intended by the following to reject the solution of the problem proposed by Prof. Kasterin, but rather to contribute to a clearing of this fundamental question.

As long as we consider Maxwell's theory only as a set

* Math. Theory of Relativity, § 32.

† Communicated by Prof. Dr. A. H. Bucherer.

‡ Phil. Mag. [7] ii. p. 1208 (1926).

§ Phil. Mag. [6] xlviii. p. 737 (1924), and l. p. 1182 (1925).

of mathematical equations, nothing forbids us to admit the possibility of any kind of discontinuities in their solutions. However, the physical interpretation of the equations leads *of necessity* to a certain *interpretation of the discontinuities*, and this brings certain difficulties.

Namely, if we say that the equations

$$\text{Curl M} - \frac{1}{c}\frac{\partial \text{E}}{\partial t} = 0, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{Curl E} + \frac{1}{c}\frac{\partial \text{M}}{\partial t} = 0, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{div E} = 0, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\text{div M} = 0, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

hold for the "free æther," while for space containing electric charges equations (1) and (3) acquire the form

$$\text{Curl M} - \frac{1}{c}\frac{\partial \text{E}}{\partial t} = \frac{\rho v}{c}, \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

$$\text{div E} = \rho, \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

we to a certain extent *define* hereby what is meant by "free æther," namely the region where $\rho = 0$.

The circumstance that (2) and (4) remain in the classical theory unaltered in any case, expresses the fact that the space (or the æther) is *always free of magnetic charges*, in other words that true magnetic charges do not exist.

In the same way (1*a*) and (3*a*) must be considered as *defining* the charge density ρ and the current density ρv, since we can observe and detect a charge and a current *only* by their action, that is *by their field*. In other words, whenever the expression

$$\text{Curl M} - \frac{1}{c}\frac{\partial \text{E}}{\partial t} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or $$\text{div E} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

differs from zero, we say that a current, viz. a charge, is present.

Now, if we consider any solution of (1), (2), (3), and (4), which at certain points or surfaces presents discontinuities, we shall generally find that (5) and (6) will be different from zero at these points or surfaces. Hence the surfaces of discontinuity will behave like surface currents or surface charges. And since, as said above, we *define* a current or a charge by *its behaviour*, we conclude that the assumption of discontinuities in the field is equivalent to the assumption

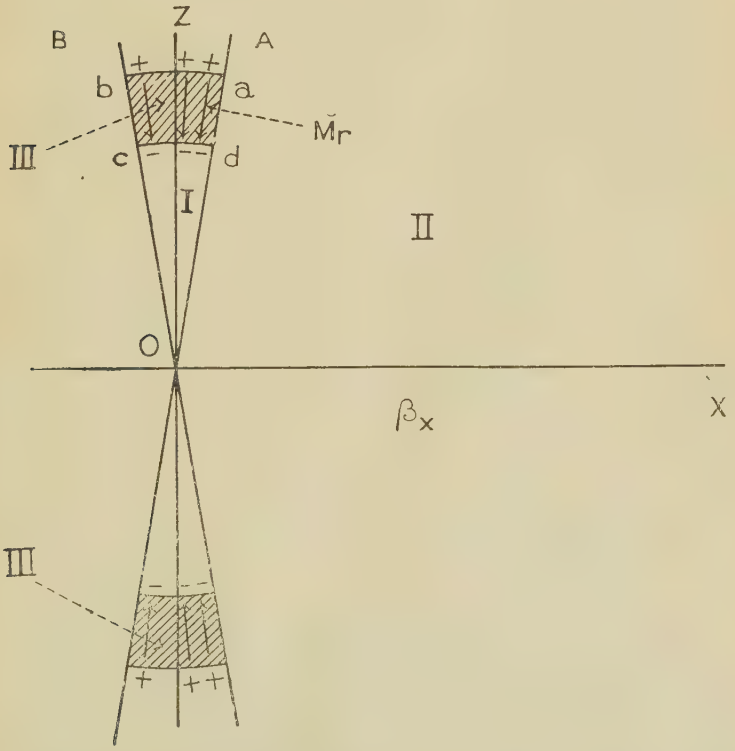
of the presence of currents and charges in this field. Hence we can no longer talk about "free æther."

To a certain extent we may say that the free æther is *per definitionem* continuous.

If we now turn to a particular case considered by Prof. Kasterin, we see that there are three kinds of discontinuities present.

First the discontinuity of the normal component of the magnetic vector at the surface of the ring, constituting the light-quantum, M_r. This physically amounts to assuming *true magnetic charges* to be carried with the quantum, or that the quantum constitutes a magnetic double layer as shown on the figure below, which is essentially the same as

Fig. 1.

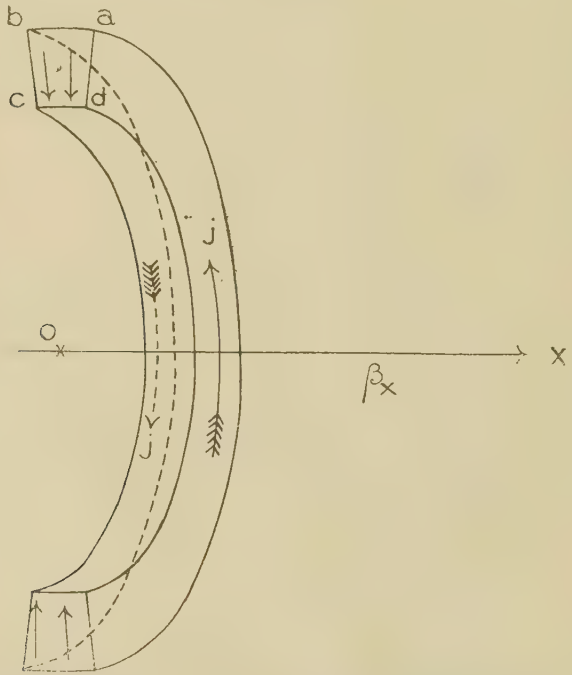


in Prof. Kasterin's paper. This, may be, is after all not such a difficulty as appears at first sight. But there is also a second discontinuity, namely that of the tangential component E_a of the electric vector at the surface *abcd*.

This causes the appearance of the surface-curl of the amount E_a on the boundary of the ring *. Hence on the surface on the ring Curl E is not equal to zero, but has a constant value. Therefore we must assume that on the surface $\frac{\partial M}{\partial t}$ is also different from zero, which would contradict the assumption, on which is based the whole deduction of Prof. Kasterin, that the field is independent of time in the system of coordinates moving with the quantum.

It seems therefore necessary to assume the existence of a *true magnetic current*.

Fig. 2.



A third discontinuity is that of the tangential component of the magnetic vector M_r on the surfaces *ad* and *bc*. This gives rise to a surface curl of M, having only the component M_a. This would correspond to a convection current having the direction indicated by the arrows *j* on fig. 2. The current on the surface *ad* has therefore an opposite direction, that of *bc*. It may be remarked that such a

* *Cf.* M. Abraham, 'Theorie der Elektrizität,' i. § 22 (Teubner: Leipzig & Berlin, 1921).

system of currents would be just equivalent to the magnetic double layer, which we must assume as shown above. Thus it seems to be unnecessary to assume true magnetic charges. But anyhow such a system of surface-currents would not account for the existence of the surface curl of E. And furthermore it is difficult to interpret physically the existence of such a surface electric convection current in the light-quantum.

For either we must assume that the light-quantum carries not only energy but also electric charge, or we must admit that the two opposite currents on the surfaces *bc* and *ad* are constituted by two opposite charges, spread continuously over the surface, moving in the same direction. But this would cause an X-component of E to appear in the region III.

Thus we see that the simple solution proposed by Prof. Kasterin does not satisfy entirely Maxwell's equations, if only we confine ourselves to "free æther" not containing any charges. It is of course not proved hereby that a more complicated solution, showing the properties of a light-quantum, may not exist. But it seems that the structure of such a light-quantum will be anyhow far more complicated than that assumed by Sir J. J. Thomson, although it may have the same general features.

The way to escape the difficulties just discussed seems to be to assume that the equations (1)–(4) hold only *inside* the ring, while on the boundary and in outside space neither (1)–(4) nor (1*a*) and (3*a*) do hold. In other words, we have to assume that there is *no field* at all outside of III. The difference should be emphasized here between the two statements : the field has a value zero, or there is no field at all. The first one describes a particular state of the æther free of disturbances ; while the second means that outside of III there is *no æther at all.* The quantum would thus be a *ring of æther, moving in absolute empty space.* This, however, would make it difficult to account for the waves accompanying the quantum according to Sir J. J. Thomson's theory.

The discussion by Prof. Kasterin on p. 1212 (*l. c.*), which is not quite clear to me, seems to indicate a similar idea. But in such a case there is no reason to consider, as Prof. Kasterin does, the solution $M=E=0$ for the regions I and II. It should be remarked that whatever the possibilities presented by such a conception are, it would lead to a radical change of our conception of charge, and would necessitate an interpretation of (1*a*) and (3*a*) which is essentially different from that made at present.

Returning now finally to the principal question, mentioned at the beginning of Prof. Kasterin's paper, as to whether the conception of light-quanta contradicts Maxwell's equations in their usual interpretation, the following may be said.

That the propagation of energy in spherical waves does not necessarily follow from Maxwell's equations is not new. C. W. Oseen * has found a solution, which represents with any required approximation an unidirectional flow of electromagnetic energy.

But even for the solutions represented by the retarded potentials, as used in the electron theory of H. A. Lorentz, the possibility of an unidirectional radiation is not excluded.

In the electron theory we are led to consider expressions of the kind :

$$\phi(x, y, z, t) = \int \frac{\psi\left(x_1, y_1, z_1, t-\frac{r}{c}\right)}{[r]}\, dx_1\, dy_1\, dz_1, \quad . \quad (7)$$

$$r = \sqrt{(x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2},$$

where the bracket denotes that the value of r has to be taken for the time $t' = t - \frac{r}{c}$.

Consider the case where ψ is of the form :

$$\psi = \theta(x_1, y_1, z_1) \sin \nu t.$$

If now the region in which θ is different from zero is small, and the distance from this region to the point x, y, z at which we seek the function ϕ is large, then we may consider r in the denominator as constant and have :

$$\phi(x, y, z, t) = \frac{1}{r} \int \theta(x_1, y_1, z_1)$$

$$\times \sin \nu\left(t - \frac{\sqrt{(x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2}}{c}\right) dx_1\, dy_1\, dz_1. \quad (8)$$

For small ν, $\sin \nu\left(t - \frac{r}{c}\right)$ varies only slowly with x_1, y_1, z_1 and therefore will be nearly constant over the region, where $\theta(x_1, y_1, z_1)$ is appreciably different from zero. We then have :

$$\phi(x, y, z, t) = \frac{\sin \nu\left(t - \frac{r}{c}\right)}{r} \int \theta(x_1, y_1, z_1)\, dx_1\, dy_1\, dz_1$$

$$= \text{Const} \frac{\sin \nu\left(t - \frac{r}{c}\right)}{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

* *Ann. d. Phys.* lxix. p. 202 (1922).

and ϕ depends only on r: that is, the field is propagated in a spherical wave.

But if ν is very large, or the region in which θ differs from zero is large, we can no longer use (9). We must go back to (8), and we see that the integral is a function in general of x, y, z; that is, ϕ depends not only on r but also on the direction. The form of this function depends on the choice of $\theta(x_1, y_1, z_1)$, and the possibility is not *a priori* excluded that ϕ will be such a function of x, y, z as will correspond to an unidirectional radiation. Now on the classical electron theory, θ and ν are always such as to justify (9). However, according to the new conception of E. Schrödinger, the electron can no more be considered as sharply limited, and in the lower quantum states the electric charge-density occupies a more extended region *. The electric charge, according to this theory, has also a complicated "internal structure." Furthermore, the light-waves are considered as difference vibrations of waves of much higher frequency. Hence, in Schrödinger's theory there is a tendency to increase the region in which θ is different from zero, as well as to increase ν. Under such conditions the transition from (8) to (9) may appear doubtful and the formula (8) to be preferred, which makes possible highly asymmetric waves, having, maybe, properties similar to light-quanta. If the fundamental waves are directed, the same will be true for waves formed by the difference vibrations.

We may probably construct a similar "energy-parcel" of the electromagnetic waves, as of the waves of Schrödinger's field-scalar ψ.

All this is, of course, very speculative, but as long as the proof of the *impossibility* of the solution of the problem, suggested here, is not given, it seems to be premature to believe in a contradiction between Maxwell's equations and the theory of directed elementary radiation.

Research Department,
Westinghouse Electric and Manufacturing Co.,
East Pittsburgh, Pa.
January 5, 1927

Note added with proof (July 20, 1927).—In the meantime a paper by G. Breit has appeared (Journ. Opt. Soc. of America, xiv. p. 374 (1927)) which in a way seems to confirm the above speculations. Breit shows that unidirectional quanta must be emitted on basis of Schrodinger's wave-mechanics, and this because of the asymmetry of the charge-motion in the atom.

* *Cf.* especially *Naturwissenschaften*, July 9, 1926, p. 664.

XLIII. *Optical Excitation of Mercury, with Controlled Radiating States and Forbidden Lines.* *By* Prof. R. W. Wood, *For.Mem.R.S.**

[Plate XIV.]

SINCE the appearance of two earlier papers on this subject† a very large amount of experimental work has been done, the publication of which has been delayed owing to the numerous discrepancies and observations requiring further study, which were continually coming to light. Most of the doubtful points have now been cleared up and a number of new and unexpected effects observed, of especial interest being the appearance of the forbidden line 2655·8 ($1S–2p_3$). That the results reported in my first paper regarding the abnormal increase in the intensity of the line 2655·13 caused by the admission of helium containing a trace of nitrogen, might be explained by the development of the forbidden line (the two being unresolved im my small spectrograph) was suggested to me by Prof. Takamine shortly after the appearance of the paper. This interesting prediction has been repeatedly verified during the past year, the two lines being clearly separated and of variable intensity ratio depending upon the conditions. With optical excitation the forbidden line comes out only in the presence of some inert gas, while Lord Rayleigh ‡ has recently photographed it in the luminous vapour outside of the zone of conduction in a mercury vapour vacuum-tube excited by a current of $\frac{1}{10}$ milliampere passed between a hot cathode and an anode plate.

The phenomena discussed in the present paper may be divided into two classes, those which merely verify Bohr's theory of absorption and emission and which can be readily explained by the energy diagram, and other effects of obscure origin which can be explained only with difficulty. It is the study of these that is likely to throw new light on the mechanism of radiation. Some of these effects I have been unable to explain up to the present time.

The apparatus used in the continuation of the work was similar to that formerly employed, except that a magnetic

* Communicated by the Author.

† R. W. Wood, "Controlled Orbital Transfer of Electrons," Proc. Roy. Soc. cvi. p. 679 (1924); Phil. Mag. October 1925.

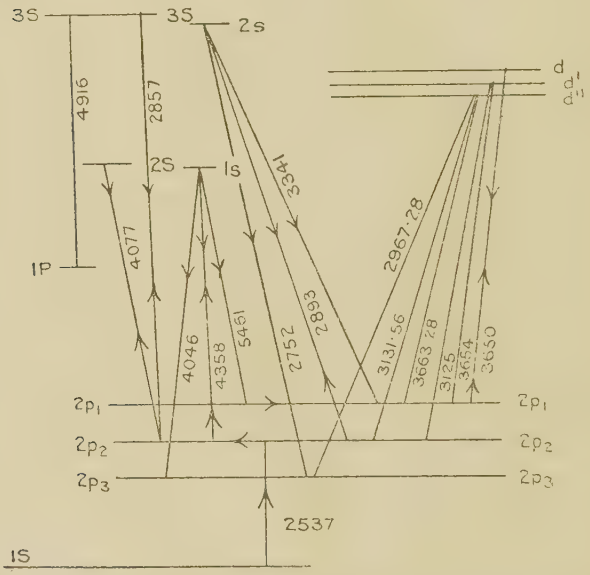
‡ Proc. Roy. Soc. cxiv. p. 636 (1927).

field was invariably used to press the discharge in the exciting mercury lamp against the wall facing the resonance tube, and a Y-tube of large bore, surmounting a barometer column of mercury, was used between the vapour pump and the resonance tube in place of a stop-cock, which prevented the contamination of the mercury vapour with vapours from grease. With this improvement the brown deposit on the inner wall of the resonance tube, resulting from prolonged illumination, which formerly gave trouble, has never appeared. It was undoubtedly carbon set free from the vapours of the stop-cock grease by contact with excited mercury atoms, but it adhered to the wall of the quartz tube so strongly that it could be removed only by polishing with pitch and rouge.

A large and very fine quartz spectrograph was used either alone or in conjunction with a quartz Lummer-Gehrke interferometer. With these instruments it has been possible to separate the close lines associated with the d'' and D levels, which were unresolved in the earlier work, a circumstance which made the interpretation of some of the results quite impossible. The resonance tube, of fused quartz, 22 cm. in length and 2·5 cm. in diameter, drawn off obliquely at the bottom to avoid reflected light and secure a black background, was mounted vertically and closed at the top with a right-angle prism of quartz, cemented with Boltwood wax, which gives off no vapour: the tapered portion at the bottom was painted black on the outside as well as the upper portion near the prism. The vertical quartz arc, with anode of tungsten and the cathode bulb immersed in running water, operated with a current of about 2 amperes was mounted close to the resonance tube, or at a sufficient distance to permit of the insertion of absorption cells of quartz filled with bromine or chlorine. The excitation of the mercury atoms in the resonance tube, which is exhausted, or filled with some gas at low pressure, takes place as follows, to cite a single typical process. By the absorption of a quantum of 2537 radiation an electron is brought to the $2p_2$ level, then by the absorption of 4358 raised to $1s$, from which it falls back either to $2p_3$ emitting 4046, or $2p_2$ emitting 4358, or to $2p_1$ emitting 5461. The latter level is metastable and the electron in this level can absorb 3650, being raised to the d level in the process. From here it falls back to $2p_1$ (its only possible transition) and 3650 is re-emitted by the vapour. These transitions are shown in fig. 1, upward pointing arrows indicating absorption transitions, downward pointing, emission.

It thus appears that 3650 is present in the optically excited spectrum as a result of *three* different processes of absorption occurring in succession. If 4358 is removed from the exciting beam by a filter of bromine introduced between the resonance tube and the lamp, the 3650 line disappears, as the second absorption process has been prevented. It is not quite clear why the electrons brought to $2p_1$ by the emission of the three lines originating on the d' d'' and D levels are not efficient for the production of 3650. On reading

Fig. 1.



over the argument advanced in my paper of two years ago I do not find it very convincing, and it may be better for the present to consider the apparent production of 3650 by electrons from 1*s* only, as a point requiring further explanation. As we shall see later on, 3650 is a line quite unique in its behaviour.

As I showed in the former papers the introduction of nitrogen into the resonance tube enhanced many of the lines to an enormous degree, by causing an accumulation of atoms with electrons on the metastable orbit $2p_3$, from which they are unable to return 1S and are hence available for the absorption of 4046, 2967, and other lines terminating on this level. This was proven experimentally by showing that 4046

was powerfully absorbed by optically excited mercury vapour in nitrogen at 3 mm. pressure. The green line 5461 is enhanced in this way as much as twenty-fold, while 4046 is enhanced only four-fold. This results from the circumstance that the vapour in the resonance tube has a high coefficient of absorption for 4046 (as a result of transfer of electrons to $2p_3$ by the nitrogen), and since the tube is viewed "end-on" the lower portions contribute very little 4046 radiation, in other words the tube shows self-absorption for this line. This is not true for the other two lines, 4358 and 5461, all portions of the tube contributing equally to the illumination. This was proved by limiting the illumination to a narrow horizontal sheet of rays, by placing a slit between the resonance tube and the lamp, in which case the increment of intensity due to the admission of nitrogen was the same for the three lines.

It is apparent that the intensity ratios of the lines emitted as a result of optical excitation depend upon a number of factors such as (*a*) the manner in which electrons on an upper level distribute themselves among lower levels (statistical distribution which governs intensity ratios); (*b*) the relative intensity of the lines in the exciting arc by the absorption of which the electrons are carried to upper levels; (*c*) transfer of electrons to metastable orbits, as by nitrogen, causing absorption of lines not normally absorbed. (*d*) An as yet unexplained action of nitrogen in causing the appearance of lines not called for by the energy diagram under the conditions of excitation, an effect probably due to the rayless transfer of electrons from upper to lower levels by collisions of the second type, or possibly, in some cases, caused by what Franck and Cario have named sensitized fluorescence: as an example excitation by bromine filtered light which raises no electrons to 1*s* owing to absence of 4358 and 4046, in consequence of which these lines and the green line are absent, all appearing, however, in great intensity on admitting nitrogen at 3 mm. pressure to the resonance tube.

(*e*) The intensity of the exciting light. This is an effect which has not yet been carefully studied. That the intensity ratio of the optically excited lines may be modified by removing the exciting lamp to a distance, thus reducing the intensity, may be seen from the following considerations.

Suppose we reduce the intensity by one half, then only one half as many electrons are brought up to $2p_2$ as before and the emission of 2537 is reduced one half, as is usual in fluorescence. All of the other lines (except 3650 and 3021) will be reduced to one quarter of their original value, as there

are but one half as many electrons on $2p_2$ available for the absorption of 4358, and 4358 has also been reduced to one half of its former value. In the case of 3650 and 3021, involving three successive absorptions, we should expect a reduction to $\frac{1}{8}$. This is a point very easily tested by experiment, but at the moment I have no data on the behaviour of 3650 when the lamp is removed to a distance. I have found, however, that a reduction of the intensity of the exciting light in this way reduces the line 2655·13 (a line involving two successive absorptions) much more than the forbidden line 2655·8 where a single absorption only is involved. On referring to my earlier paper I find an observation recorded which is in agreement with this view. It was found that, by applying a magnetic field to the arc, the intensity of 2537 in the optically excited vapour was increased four-fold : the lines 5461, 4358, 4046, 3663, 3654, 3131, 3125, and 2967 (all involving *two* absorptions) were increased eight-fold and the line 3650 (involving three absorptions) was increased sixteen-fold. This is the converse of the case just considered, the application of the magnetic field (by abolishing self-reversal of the exciting lines), corresponding to *increasing* the intensity of the exciting light. It was found also that 3650 was partially reversed in the arc in the absence of a magnetic field, *i. e.* the field caused its enhancement in the exciting light. The question will be more fully taken up in a subsequent paper.

The tremendous increase in the intensity of the optically excited spectrum, caused by the admission of a gas, nitrogen in particular, which was mentioned in the earlier papers has been more fully investigated. Results conflicting with earlier observations and not always easy to duplicate were obtained.

These discrepancies were finally traced to the circumstance that the increment of intensity of the emitted light caused by the nitrogen varied along the path of the exciting beam. Consistent results were obtained as soon as an image of the cross-section of the resonance tube was projected on the slit of the spectroscope with a quartz-fluorite achromat. The light is most intense along the side of the resonance tube facing the lamp, falling off to less than one quarter of this value in some cases as we pass along the diameter to the opposite side of the tube. This is, of course, due to the absorption of the exciting radiations. The decrement in intensity is not the same, however, for all of the emitted spectrum lines, since the coefficient of extinction is not the same for all of the exciting radiations.

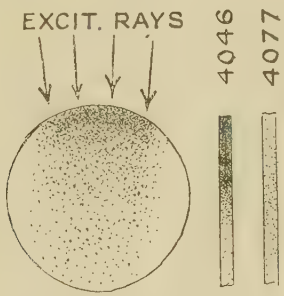
The luminosity distribution of the light in the image of

the cross-section of the tube on the slit and in the lines 4046 and 4077 is shown in fig. 2.

In the earlier investigations no lens was used to form an image on the slit, the collimator being simply pointed down the resonance tube (seen end-on in the right-angle prism which surmounted it). Diaphragms were arranged so that no light scattered by the tube walls entered the spectroscope but, with the frequent re-adjustments made, it is obvious that the spectroscope must sometimes have received light from the more strongly illuminated side of the tube, and sometimes from the less intense portion, therefore no consistency could have been expected in view of the more recent observations.

The photograph reproduced on Plate XIV. fig. 1 was made in this way and will be referred to later.

Fig. 2.



It is evident that with so many factors operating simultaneously it is very difficult to discuss the results of the experiments: facts come to light slowly as a result of comparing a large number of photographs, and little can be done until long experience has made it possible to visualize the energy diagram as a chess-player visualizes the board.

If the total light of the arc is employed matters are almost hopelessly complicated, and we will begin with a discussion of the results obtained with the bromine-filtered excitation, in which case the distribution of electrons over the $2p_1p_2p_3$ levels from $1s$ does not occur. For the present we will confine ourselves to the transitions between the $dd'd''$D and the $2p_1p_2p_3$ levels, together with the 1P level to which electrons may pass from the d'D levels with emission of the yellow lines.

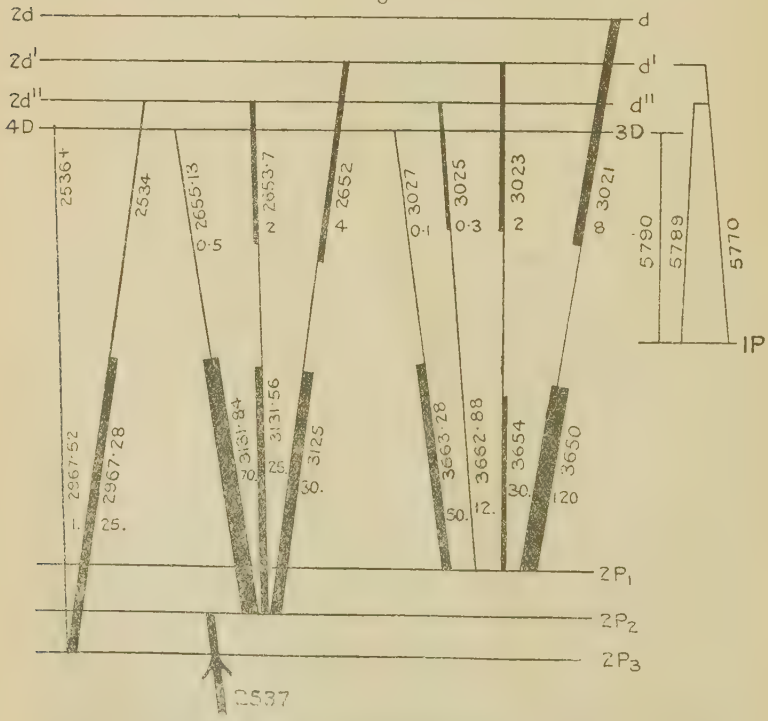
For a discussion of the results it is clear that we must have a record of the relative intensities of the exciting lines emitted by the arc; such a table was given in the earlier

paper, but at the time only the sums of the intensities of the close lines originating on the d'' and D levels were available. As very conflicting statements regarding these intensities were found in the literature, determinations were made with the arc actually employed in the work (*i. e.* water-cooled, and with magnetic field operating). The lines were photographed with a 21 foot concave grating with different times of exposure for each pair of lines. The results are given in the following table, heavy type indicating the bright lines for convenience of reference.

(2D–$2p_1$)	**3663·28**	4 times intensity of 3662·88	(d''–$2p_1$).
(2D–$2p_2$)	**3131·84**	3 „ „	„ 3131·56 (d''–$2p_2$).
(2D–$2p_3$)	2967·52	$\frac{1}{20}$ of „	„ **2967·28** (d''–$2p_3$).

With the lamp warm, 3131·56 becomes brighter than 3131·84, which reverses. The extreme faintness of 2967·52 is to be especially noted.

Fig. 3.



A diagram of the energy levels involved and the transitions with which we shall deal is given in fig. 3. As an aid in

visualizing the effects to be expected from given transitions, I have indicated roughly the intensities of the lines in the exciting arc by the widths of the lines joining the levels. As a further aid I have found it advantageous to represent the $d\,d'd''$ and $2d\,d'd''$ levels by the same lines. On the lower portions of the vertical lines joining the energy levels we find the data for the transitions from $2p_1p_2p_3$ to the d levels, and on the upper portions the data for the corresponding transitions to the $2d$ or upper levels. The actual intensities of the lines are given just below the wave-lengths. This type of diagram may seem confusing at first, but it enables us to see at a glance which lines are analogous (*i. e.* 3125 is analogous to 2652), a matter of importance in the study of the action of various gases on the electron transfers.

We will begin with a critical study of the effects of nitrogen on the radiation excited by bromine-filtered light, this being a comparatively simple case. The results are given in the following table for nitrogen at two different pressures, the numerals following the wave-lengths indicating the increment in intensity caused by the nitrogen (in comparison with the intensities emitted when the mercury vapour is *in vacuo*). The third column gives the values when no bromine filter is used.

	Nit. 4 mm.	Nit. 0·25 mm.	Nit. 0·25 mm. (no bromine filter).
3663	8	2	2
3654	2	1	1
3650	30	2	−2
3131	8	4	4
3125	2	1	1
2967	8	16	6

In this table 1 means that the intensity is unchanged, 8 that it has been increased eight-fold, and −2 that it has been *reduced* to $\frac{1}{2}$ of its value for vacuum.

Actual intensities of two of the lines were as follows : —

	2967.	3131.
Hg *in vac.*	1	4
Hg in Nit. 3 mm.	8	32
„ „ „ ·25 mm. ...	16	16

Referring now to the diagram fig 3, we will see how

many of the above changes can be explained. For mercury *in vacuo* we have absorption from the $2p_2$ level only, *i. e.* lines 3131·84, 3131·56, and 3125. For the present we shall treat the two former as a single line, since they were unresolved in the spectrogram from which the above photometric measurements were made. As a result of 3131 absorption we have 2967, 3131, and 3663 emission, while 3125 absorption gives 3125 and 3654 emission. Line 3650 is absent in so far as the above processes are concerned, though a trace of it may appear on the plate as a result of absorption of 3650 (not entirely removed by bromine filter) by electrons brought to $2p_1$ by the emission of 3663 and 3654 above referred to. Line 2967 will be relatively weak since its component from d'' results from electrons carried to d'' by the relatively weak line 3131·56, while the component from 3D is vanishingly weak since the probability of the transfer 3D–$2p_3$ is very small (as shown by the faintness ($\frac{1}{20}$) of this line in the arc.

The addition of nitrogen at 0·25 mm. increases the intensity of 2967 sixteen-fold, 3131 four-fold, and 3663 two-fold.

No change occurs in the case of 3125 and 3654, which indicates that there are as many atoms with electrons on the $2p_2$ level as before the introduction of the nitrogen, in spite of the large number with electrons on $2p_3$.

We will now calculate the expected intensities resulting from the nitrogen.

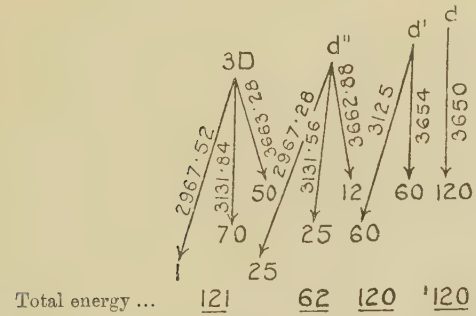
The relative intensities of the exciting lines involved, obtained by combining the relative values given for the d'' and 3D components given above with the relative values recorded in the former paper, are given in the following table :—

From upper level.		Int.
3D	3663·28	50
d''	3662·88	12
d'	3654	60
d	3650	120
3D	3131·84	70
d''	3131·56	25
d'	3125	60
3D	2967·52	1
d''	2967·28	25

The distribution of energy from the $d\,d'\,d''$3D levels to the

$2p_1p_2p_3$ is represented in the following diagram (fig. 4), the total energy from each upper level being recorded below.

Fig. 4.



We first calculate the intensity ratios to be expected for mercury *in vacuo*, taking the sum of the portions contributed by the absorption of 3131·84 and 3131·56. If we consider that the energy expended in raising electrons from $2p_2$ to 3D and d'' by the absorption of these two lines is proportional to the intensities of the lines in the exciting arc we have 3131·84 contributing energy 70, which is divided among the levels $2p_3p_2p_1$ in the proportion $\frac{1}{2}$, 40, and 30 (1, 70, 50, on diagram for 3D), and 3131·56 contributing 25, which is divided in the proportion 10, 10, 5 (25, 25, 12, on diagram for d''). Adding the values for each of the $2p$ levels gives us the following intensity ratios for the (double) lines :—

D d''	Op. Excit.		Hg. Arc.	
$\frac{1}{2}+10=10{\cdot}5$	1	2967	26	1
$40+10=50$ or	5	3131	95	or 3·6
$30+5=35$	3·5	3663	62	2·4

If nitrogen at 0·25 mm. is added, we find that the line 2967 has increased in intensity 16-fold, and from this we can calculate the expected increments of the other lines, thus :—

Assume a sufficient number of atoms with electrons brought by the nitrogen to the metastable level $2p_3$ to give a sixteen-fold increase of (the double line) 2967 by the absorption 2967·28, which raises the electrons to the d'' level. The diagram (fig. 4) for the redistribution among the $2p$ levels shows that if we contribute intensity 15 to 2967 (which may be considered as having a value 1 as a result of

the absorption of 3131 by atoms unaffected by the nitrogen) we must also contribute intensity 15 to 3131·56 and intensity 7·5 to 3662·88. This gives us for the intensities :—

		In Nit.	Vac.
2967	1 +15	= 16	1
3131	5 +15	= 20	5
3663	3·5+ 7·5	= 11	3·5

The calculated increment for 3131 is 4, which agrees exactly with the observed four-fold increment. For 3663 the agreement is not so good, a three-fold increment calculated and a two-fold observed. It should be noted that, in setting the absorptions proportional to the intensities of the lines in the exciting arc, we have assumed that the absorption coefficient of the excited vapour for the lines in question is the same. This is of course not justifiable, so that the above computations are to be regarded merely as a rough attempt to follow out the changes in intensity of the various lines.

With 4 mm. of nitrogen in the resonance tube all three lines appear enhanced to the same degree, namely eight-fold. It seems probable that this is, in part at least, the result of the strong absorption of 2967 by the atoms with electrons on $2p_3$, the weakening of this line in comparison with others being analogous to the smaller increment in intensity of 4046 in comparison with 4358 and 5461, previously alluded to.

The enormous increment (thirty-fold) of 3650 results probably from electrons brought down from higher levels to the d level by collisions of the second type, or possibly by something analogous to the sensitized fluorescence of Franck and Cario. The very small value of its intensity *in vacuo* is responsible for the abnormally large value of the increment.

In nitrogen at 0·25, however, the increment is only two-fold. Here also I believe the enhancement to be due to the same cause.

If no bromine filter is used, which causes electrons to be scattered over the $2p_1p_2p_3$ levels from $1s$, the presence of 0·25 mm. of nitrogeh causes a two-fold *decrease* in the intensity of 3650, and as we shall see presently this decrease may be as much as four-fold with nitrogen at a lower pressure, 0·05 mm. Referring to the diagram fig. 4, it is seen that we can predict the effect of nitrogen traces on the relative intensity of lines originating on the D and d'' levels.

In vacuo 3131·84 must be much brighter than 3131·56, since it is much brighter in the exciting light, and of all the

electrons raised to D by its absorption, only a very few fall to $2p_3$ (as we know from the small intensity of 2967·52 in the arc). Of the electrons raised to d'' by the absorption of the fainter line 3131·56, many fall to $2p_3$, and are unavailable for the re-emission of 3131·56.

With nitrogen in the tube, however, we have powerful absorption of the strong line 2967·28 which contributes to the emission of 3131·56, while very few electrons are carried from $2p_3$ to D owing to the faintness of the 2967·52 line. Nitrogen should thus enhance 3131·56 enormously.

This prediction was verified by photographing the optically excited vapour with a quartz Lummer-Gehrke plate (interferometer) used in conjunction with a quartz spectrograph, the horizontal fringe system formed by the plate being projected on the wide-open slit of the spectrograph by means of a quartz-fluorite achromatic lens of 40 cm. focus. With the mercury vapour *in vacuo* (Pl. XIV. fig. 4 *a*) the line 2967 does not appear and 3131·84 has about the same intensity as 3125, the displacement of the two fringe systems by the spectrograph being quite evident in the photograph. A mere trace only of 3131·56 appears.

With nitrogen at a very small fraction of a millimetre 2967·28 appears, and 3131·84 and 3131·56 have the same intensity (fig. 4 *b*).

With nitrogen at 1·5 mm. (fig. 4 *c*) 3131·56 is many times brighter than 3131·81, while 2967 is no brighter, if as bright as in case *b*. This is due to the "self-reversal" of 2967·28 by the atoms with electrons on $2p_3$, a phenomenon already described in the case of the line 4046.

All of the above changes are what we should expect from the diagram. In the case of the yellow lines, however, we find a difficulty.

The Yellow Lines.

Observations made visually of the relative intensity of the two yellow lines (by opening the slit of the spectroscope until the two monochromatic rectangles touched each other) showed that, with mercury *in vacuo*, the lines had the same intensity, but that in nitrogen the 5790 line appeared to have about double the intensity of 5770. The enhancement of 5790 was much greater with the exciting light filtered through bromine than when the total radiation of the arc was employed; this indicates that the enhancement results from the electrons on $2p_3$ (brought there by the nitrogen), the removal of 4046 by the bromine leaving more atoms available for the absorption of 2967·28.

Referring now to the diagram, fig. 3, we find a difficulty

at once, since the line 5790 originates on the 3D level, to which electrons can be brought from $2p_3$ only by the absorption of 2967·52, which has only about $\frac{1}{20}$ of the intensity of 2967·28. The absorption of this latter line carries electrons to d'', and the mercury line 5789 originates on this level, but it is normally so faint that it is difficult to believe that it is responsible for the enhancement observed. The lines 5789 and 5790 would not appear resolved in the spectroscope used. To settle this matter it will be necessary to photograph the yellow lines with the Lummer plate, a matter of some difficulty owing to the long exposure required. If it should turn out that 5789 was in reality greatly enhanced, the phenomenon might perhaps be analogous to the development of the forbidden line 2655·8 which does not appear at all in the arc or spark spectrum, but which comes out in the optically excited spectrum of mercury in nitrogen at 4 mm. with an intensity comparable to that of the other lines. This being the case, it is barely possible that the transfer ($1P$–$2d''$), which normally is extremely infrequent, may be greatly facilitated. It is, perhaps, more likely that the nitrogen transfers electrons from d' to 3D in a manner analogous to the transfer from $2p_2$ to the metastable level $2p_3$. Such a transfer would decrease the intensity of 5770 and increase that of 5790. It would also tend to decrease 3125 and increase 3131·84. I have frequently detected a decrease of 3125. The slight increment of 3131·84 due to this assumed action of nitrogen would be completely offset by the enormous increment of 3131·56 (resulting from absorption of 2967·28), so that the results obtained with the Lummer plate are not in opposition to this hypothesis. It is possible, too, that the nitrogen transfers electrons from d'' to 3D.

If a filter of chlorine is used in conjunction with bromine no visible light is emitted by the vapour, the excitation being confined to radiations below 2967. The d3D levels are now free of electrons, but if nitrogen at 3 mm. is added all of the missing lines appear, and the yellow lines now have the *same intensity* (as is the case with mercury *in vacuo* excited by 3131·84 and 3125). This shows that an emission caused by electrons brought down to d' and 3D from upper levels does not give an enhancement of 5790.

The enhancement of 5790 is not much in evidence until the pressure of the nitrogen is over 2 mm., while ·5 mm. is sufficient to greatly enhance all lines depending upon absorption from the $2p_3$ level, which makes it appear probable that

the nitrogen either transfers electrons from d'' to 3D, in which case 5790 will be enhanced, or increases enormously the probability of the 1P–d'' transfer which will increase the intensity of 5789.

Development of the HO band: Sensitized fluorescence.

As reported in the earlier papers, the optical excitation of mercury vapour in dry nitrogen gives, in addition to the mercury lines, strong bands, one of which in the vicinity of the mercury line 3125 has been definitely identified with the so-called "water-band" emitted by the oxy-hydrogen flame, and other sources of light in which water vapour is present. This band is now attributed to an HO molecule.

A photograph of the band excited by the light of the mercury arc is reproduced on Plate XIV. fig. 3, in coincidence with the spectrum of an oxy-coal-gas flame. The two mercury lines 3125 and 3131 appear within the band. With continued exposure to the light of the arc the water-band gradually fades away and is replaced by an equally complicated band in the same region but extending beyond the water-band on the short wave-length side.

The distribution of intensity among the lines forming the band is very different in the two types of excitation, a matter which is being investigated in collaboration with Prof. F. W. Loomis and will be reported in a subsequent paper. It is of some interest in view of recent work on the origin of band spectra.

The "Forbidden" line 2655·8 (1S–$2p_3$).

The appearance of this line with an intensity equal to that of its near neighbour 2655·13 ($2p_2$-4D) is a matter of great interest.

I have already mentioned the conditions under which it appears (mercury vapour in nitrogen or a mixture of helium and nitrogen). As yet no study has been made of the conditions most favourable to the appearance of the line, or whether it can be brought out by any other gas than nitrogen. It is shown on the photograph (Pl. XIV. fig. 2) at the right of the group 2652–2655. It apparently does not attain any considerable intensity until the pressure of the nitrogen is sufficient to bring out the "water-band" strongly. The other forbidden line 2270 (1S–$2p_1$) I have not yet observed. It is doubtful whether it can be found in this way, as the number of atoms with electrons on the $2p_1$ orbit

is probably small in comparison with those with electrons on $2p_3$.

As I have stated in the section on the "water-band," continued exposure causes the HO band to disappear and another band of unknown origin (a compound molecule of N and H perhaps) to take its place. The forbidden line becomes weaker when this state is reached, probably due to the presence of hydrogen set free by the action of the excited mercury atoms on the water-vapour. This liberation of hydrogen I have observed with mercury vapour *in vacuo*, sealed from the pump by the mercury Y-tube. The pressure rises quite rapidly as a result of illumination by the Hg arc, and the liberated gas is shown to be hydrogen by a small spectrum tube in circuit with the resonance tube. The oxygen probably combines with the mercury, for I have observed that if air at 1 mm. pressure is admitted to the resonance tube, the emitted light is very feeble at first, rising, however, to the full intensity which it would have in pure nitrogen after a few minutes of illumination.

The intensity of the forbidden line appears to be greater under the conditions specified than by electrical excitation, probably as a result of an enormous concentration of atoms with electrons on $2p_3$. I have hopes of being able to photograph the fine structure of this line with the Lummer plate. If this can be done it will throw a good deal of light on the nature of the 1S level, as the fine structure of but one other line involving this level is known (2537).

Development of Absent Lines by Nitrogen.

If a combined filter of chlorine and bromine is placed between the lamp and the resonance tube, the vapour is excited only by lines of shorter wave-length than 2750.

If the mercury vapour is *in vacuo* we have an invisible emission comprising lines originating on the upper $2d$D levels to which electrons are carried from $2p_2$ by the absorption of 2652, 2653, and 2655.

If nitrogen at 3 mm. is added to the vapour all of the arc lines are emitted with greater or less intensity, which shows that electrons are either brought down from the upper levels to the lower, or carried up from the $2p$ levels by the nitrogen (activated perhaps by the excited mercury). There seems to be no experimental way of settling between the two processes, for there is no way of bringing electrons up to the $2p$ levels from 1S without at the same time raising

them to the upper levels by the absorption of 2534·8 ($2p_3$–$3d''$) and $2536 \pm (2p_3$–3D) (the latter line has never been observed on account of its proximity to the $1S$–$2p_2$ line 2537). To separate 2537 from these lines for illumination is impossible.

The relative intensities of lines developed in this way will depend upon how the electrons are distributed by the nitrogen among the levels intermediate between the $2p$ levels and the upper 2 dD levels. Self-absorption in the resonance tube may also operate for some lines, as we have electrons on the $2p_2p_3$ levels, as a result of the primary excitation by 2537 and the presence of nitrogen which transfers electrons from $2p_2$ to $2p_3$

In the absence of this self-absorption, as when employing a very thin layer of radiating vapour, we should expect the intensity ratio of lines originating on the same level (4046–4358, 5461 for example) to be the same for all types of excitation and for all conditions. It was found that the lines 3663—3131—2967 were in the ratio 25—50—25, while in the arc and by optical excitation the ratio is 25—95—62.

These ratios are for the lines from D and d'' *unresolved*, as photographed with the spectrograph. Referring to the distribution diagram (fig. 4), we see that the ratio 25:50:25 will be very nearly realized if we consider that the D level contributes only $\frac{1}{4}$ of its usual amount, *i.e.* to the intensities from d'', or 25, 25, 12, we add $\frac{1}{4}$, 17·5, and 12 instead of 1, 70, and 50—obtaining roughly 25, 43, 24.

If this is the correct explanation it means that the nitrogen favours the d'' level in its distribution, the D level receiving only $\frac{1}{4}$ of its usual quota. On one plate, taken with a filter of chlorine only, the three lines in question had the same intensity, 3125 and 3654 (from d') were equal and brighter, while 3650 (from d) was still brighter. This matter will be further investigated as it appears to be of some importance.

The effect of the nitrogen in bringing out the various lines of the spectrum with a chlorine-bromine filter was determined by giving an exposure of 1 hour with the filters interposed and 4 mm. of nitrogen in the resonance tube, and then a series of exposures with the mercury *in vacuo* and no filters, of exposure times 25 mins., 3 mins., 90, 45, 22, 11, and 6 seconds. The slit was opened fairly wide and the densities of the lines in the two cases compared. The numbers following the wave-lengths are the exposure times in seconds, for Hg *in vacuo* and no filter, necessary to give a density equal to that given by an hour's exposure (3600 secs.) with filters and nitrogen in the tube.

1*s*	5461	22
1*s*	4358	22
1*s*	4046	11
2S	4077	90
d″D	3663	22
d′	3654	22
d	3650	45
2*s*	3341	1500
d″D	3131	45
d′	3125	22
2*d*	3021	90
d″3D	2967	22
2*s*	2893	1500
3S	2856	3000
	2803	missing
2*s*	2752	1200
4D	2655	3000
2*d*″	2653	1500
2*d*′	2652	45

The blue-green line was observed visually to come out with considerable intensity with nitrogen at 4 mm., both with and without a bromine filter. Absorption from the $2p_3$ level cannot help in bringing out this line (see diagram, fig. 1), consequently we must ascribe it to electrons brought to 3S from other levels by the nitrogen.

If we were exciting the mercury with 2537 alone, the numbers following the wave-lengths might be taken as representing the efficiency of the nitrogen in developing the lines, allowing of course for self-absorption in the tube, which as in previous cases weakens 4046 with respect to 4358 and 5461 and gives us a diminished efficiency which is of course not real. The very high numbers above 1000 result from the circumstance that direct optical excitation is operating in these cases, as the filters do not absorb the lines below 2800. Thus the lines 3341, 2893, and 2752 result from the absorption of the 2752 radiation by electrons on the $2p_3$ orbit, brought there by the nitrogen.

The line 4077 ($2S–2p_2$), for which the efficiency is 90, is not optically excited however, which seems to indicate that the nitrogen favours the 2S level. The same appears to be true for *d* and 2*d* levels (3650 and 3021). The large value for 2856 indicates that it must be optically excited, though the chlorine is fairly opaque here.

Very surprising are the last three cases for the closely adjacent $2d'd''$4D levels. These lines are all optically excited, and we should expect that the relative intensities would be

the same as those observed without the filters. We find, however, that in this case the nitrogen appears to be 33 times as efficient in developing 2653 as in bringing out 2652 and 66 times as efficient for 2655. The intensity increments observed without the filters for several other gases for the three lines were :

	Nit. 3 mm.	CO 0·045 mm.	Argon 1 mm.
2652	1	1	1
2653	4	12	10
2655	1	1	1

In the nitrogen case we have, with the filters (as shown by the diagram, fig. 3), an emission resulting from the absorption of 2534·8 from the $2p_3$ level, and this absorption is the only one operating on the electrons on $2p_3$. Without the filters, however, we have electrons removed from $2p_3$ by the very powerful 4046 and 2967 radiations and scattered over the $2p_1 p_2 p_3$ from the upper levels to which they have been raised. This may account for the enormous difference observed, but the matter requires further investigation with control experiments. The still greater increase in the case of 2655 is probably due to the development of the 2655·8 forbidden line $1S–2p_3$ mentioned elsewhere.

The Decrease of Intensity of Certain Lines by Gases at Low Pressure.

Certain lines are decreased in intensity in a remarkable manner by the admission of a gas at extremely low pressure to the resonance-tube.

The most interesting case is that of the line 3650, which is decreased four-fold in intensity by nitrogen at 0·05 mm. while all the other lines are either enhanced or unaffected. Photographs showing this effect are reproduced on Plate XIV. fig. 1, A showing the group 3650–3663 for mercury *in vacuo*, and B the same group and same conditions of illumination with 0·05 mm. of nitrogen in the resonance tube. The line 3650, which in A has about four times the intensity of 3654, has faded in B to an intensity exactly equal to that of 3654. As the nitrogen pressure increases the reduction becomes less and finally there is a considerable increment, the changes being as follows :—

Nitrogen pressure...	2	1·25	·43	·2	·1	·05 mm.
Intensity increment or decrement.....	2	1·5	1	−2	−4	−5

A similar decrease of intensity was found for the line 3021 (the line analogous to 3650) from the upper 2 *d* level. The two *d* levels thus appear to be sensitive to very small traces of nitrogen.

A similar decrease in the intensity of 3650 was observed with argon and helium, though not as great as with nitrogen. With CO at 1·25 mm. a six-fold reduction was observed for 3654, 3650, and 3125, while 4358, 3131, and 2967 were unaffected. As the action of carbon monoxide appeared to be peculiar, we will take it up more in detail,

The action of Carbon Monoxide and Argon.

The effect of CO at two different pressures on the various lines is shown in the following table, together with the effect of argon.

	CO ·045 mm.	CO 1·25 mm.	Argon 1 mm.
4358	−1·5	1	3
4077	−2	..	1
4046	−1·5	−2	2
3663	1	−2	2
3654	−2	−6	1
3650	−5	−6	−1·5
3341	1·5	...	2·5
3131	3	1	4
3125	−3	−6	1
3023	−2	...	1
3021	−2	−3	2
2967	3	1	4
2893	1	...	2·5
2653	12	...	10
2652	1	−2	1

The increment of 3131 and 2967 by CO at ·045 mm. indicates that electrons have been brought to $2p_3$ by the gas. They appear, however, to be inoperative in causing absorption and re-emission of 4046, since the lines from 1*s* are all reduced in intensity. The line 2967 is evidently absorbed, for we have a threefold increment of the lines from d''. It is the behaviour of the 2653 line, from $2d''$, however, which is most striking. This is increased in intensity *twelve-fold*! and results from absorption of 2534 from the $2p_3$ orbit.

The only interpretation of these results that I am able to give at the moment is that, with CO, we have electrons on

$2p_3$, but the probability of absorption from this level with its consequent re-emission decreases as the wave-length increases, in other words quanta of a large energy value (as 2536) are absorbed in great numbers, while those of smaller energy value (as 2967) are absorbed to a lesser degree, and those of still smaller energy (as 4046) not at all. It will be necessary to study the absorption of the excited mercury vapour in CO with the Lummer plate to test the correctness of this interpretation. This will be investigated.

Effect of Nitrogen at Different Pressures.

The effects of nitrogen at different pressures were investigated both with the exciting lamp water-cooled and with magnetic field, and with the the lamp warm and without field. Very different results were obtained in the two cases, which shows how careful we must be in specifying the conditions under which the exciting lamp operates. For example, with the lamp slightly warmed and no field 3650 showed no decrease in intensity with low-pressure nitrogen. It is moreover necessary to make the photographs by projecting an image of the "end-on" resonance tube on the slit of the spectrograph, and make the photometric comparisons with the portion of the image where the light enters the tube. If we compare the increments of intensity for the vapour near the point of exit for the exciting light very different values are obtained, as I have previously pointed out, due to the fact that some of the absorbed rays are rapidly quenched while traversing the tube, while others are not.

The increments and (decrements) obtained with nitrogen over a wide range of pressure are given in the following table.

	Nitrogen pressure:							
	11	4	2	1·25	0·43	0·2	0·1	0·05 mm.
5461	8·5	13	15	12	6	4	2	1·5
4358	6·5	12	12	12	6	4	2	1·5
4046	3	3	4	3	2	2	2	1·5
3663	1·5	3	4	4·45	3	2	1·3	1
3654	1·5	...	1·5	1·5	1	1	1	1
3650	−1·5	3	2	1	1	−2	−4	−5
3131	2·7	6	8	9	6	4	2	2
3125	−1·5	1	1	1	1	1	1	1
2967	1	2·5	4	6	8	8	6	1

These values are to be regarded as provisional however.

It has not been considered worth while, up to the present, to make accurate photometric measurements, owing to the large discrepancies found with rough measurements. Now that the causes of these have been found, accurate measurement will be made.

The much greater increments reported in the earlier paper (thirty-fold for 5461 for example) were found to be due to the circumstance that a magnetic field was not used in these cases. The "core" of the exciting line being removed by absorption, we have a comparatively feeble excitation of mercury *in vacuo*. The addition of nitrogen, by broadening the lines in the usual manner, enables the vapour to utilize frequencies slightly greater and less than the frequency at the centre of the line, and hence causes a greater increment of intensity than in the case of excitation by lines in which the "core" is the most intense part. In other words, the larger increment is seen to be due to the circumstance that, with partially reversed exciting lines, the optical excitation is feeble with mercury *in vacuo*, and it is in comparison with this feeble luminosity that we measure the increment.

Observations made recently under the same conditions and consecutively, with and without the magnetic field, on the increments due to nitrogen at 2 mm. for the region of the resonance-tube where the exciting beam enters, and also at the region of exit, are given in the following table.

	Without mag. field.		With mag. field.	
	Entrance.	Exit.	Entrance.	Exit.
5461	24	18	9	9
4358	18	12	6	6
4046	6	6	2	3
3650	7	4·5	2	1
3131	12	9	6	4·5

XLIV. *A Note on the Structures of the Arc Spectra of Elements of the Oxygen Group. By* Professor J. C. McLennan, *F.R.S.*, A. B. McLay, *Ph.D.*, *and* J. H. McLeod, *M.A.**

I. *Introduction.*

THE structure of the arc spectrum of elements of the oxygen group—*i. e.*, O, S, Se, Te, or Po—should, according to the Pauli-Heisenberg-Hund theory, be characterized chiefly by the terms that are given in Table I. and in Table II. In these tables, it will be

* Communicated by the Authors.

TABLE I.

	Electron Configuration.		Term Types.		
	$n_1\ n_2\ n_3 \ldots$	$(n+1)_1\ (n+1)_2 \ldots$	A.	B.	C.
$O_{II}\ S_{II}$ ...	2 3 —	— —	n^4S	n^2D	n^2P
$O_I\ S_I$	2 4 —	— —	n^3P	$n^1\overline{D}$	$n^1\overline{S}$
	2 3 —	1 —	$(n+1)^5S$ $(n+1)^3S$	$(n+1)^3D$ $(n+1)^1D$	$(n+1)^3P$ $(n+1)^1P$
	2 3 1*	— —	n^5D n^3D	$n^3G\ \ n^3F\ \ n_B{}^3D\ \ n_B{}^3\overline{P}\ \ n_B{}^3S$ $n^1G\ \ n^1\overline{F}\ \ n_B{}^1D\ \ n_B{}^1P\ \ n_B{}^1S$	$n^3F\ \ n_C{}^3D\ \ n_C{}^3\overline{P}$ $n^1\overline{F}\ \ n_C{}^1D\ \ n_C{}^1\overline{P}$
	2 3 —	— 1	$(n+1)^5P$ $(n+1)^3P$	$(n+1)^3F\ \ (n+1)_B{}^3\overline{D}\ \ (n+1)_B{}^3P$ $(n+1)^1F\ \ (n+1)_B{}^1D\ \ (n+1)_B{}^1P$	$(n+1)_C{}^3\overline{D}\ \ (n+1)_C{}^3P\ \ (n+1)_C{}^3\overline{S}$ $(n+1)_C{}^1\overline{D}\ \ (n+1)_C{}^1P\ \ (n+1)_C{}^1\overline{S}$

* In the oxygen atom there is no orbit n_3 where $n=2$. Each term in this row should therefore have the prefix $(n+1)$ for O_I.

TABLE II.

	Electron configuration.	Term Types.
	n_1 n_2 ...	D.
O_{II} S_{II} etc.	1 4	$n\,^4P$ $n\,^2P$ $n\,^2\overline{D}$ $n\,^2\overline{S}$
O_I S_I, etc.	1 5	$n_D\,^3\overline{P}$ $n_D\,^1\overline{P}$

seen, configurations are given of the six outermost electrons of the neutral atoms, and along with them the type terms to which they give rise. Configurations are also given of the five outermost electrons of the singly ionized atoms in their normal state, together with the type terms corresponding to them. From these latter the terms of the arc spectrum were derived. The number "n" is to be understood as having the values 2, 3, 4, 5, and 6 for O, S, Se, Te, and Po respectively. The terms of the arc spectrum are divided into four groups or systems, three being given in Table I. in the columns designated by A, B, and C, and the fourth in the column in Table II. designated by D. These groups are identified by the particular series limits involved. Each term has been designated in the tables in such a way that it can be unambiguously referred to in the succeeding discussion. It should be mentioned that the deep-lying term $n\,^3P$ is the first member of each of the three term sequences of which $(n+1)_A\,^3P$, $(n+1)_B\,^3P$, and $(n+1)_C\,^3P$ are respectively the second member. The term $n\,^3P$ is therefore common to the three systems A, B, and C. Similarly, $n\,^1\overline{D}$ is common to systems B and C, but $n\,^1\overline{S}$ belongs only to system C. Although there are really four systems possible in Table II., one based on each term $n\,^4P$ etc. of the first spark spectrum, the two terms of the arc spectrum given in the table are the only ones that are likely to be observed. The four systems have been grouped therefore for convenience into one—namely, system D.

Higher series members of any term system in Tables I. or II. are obtained when the excited electron occupies an orbit of higher total quantum number—say, $(n+x)$,—and the corresponding terms will then be designated by this number as prefix.

II. *Previous Investigations.*

The arc spectra of oxygen [1, 2, 3, 4], sulphur [1, 3, 4, 5], and selenium [1, 4] have been analysed to some extent by other investigators.

In O_I the following terms have been identified :—$2\,^3P$; $(n+1)\,^3S$, $n=2$ to 10; $(n+1)\,^5S$, $n=2$ to 9; $(n+1)\,^3P$, $n=2$ to 4; $(n+1)\,^5P$, $n=2$ and 3; $(n+1)\,^3D$ and $(n+1)\,^5D$, $n=2$ to 9. It is therefore evident that the term system A is very completely known. No terms in the term systems B, C, and D have been finally identified as yet, but it seems that as there are a number of unidentified triplet and singlet lines [1, 2] that undoubtedly belong to O_I these should be found to lead to terms in these systems. It is interesting to find that Hopfield in a recent note has brought forward evidence that indicates that the famous auroral green line is a so-called forbidden line corresponding to an electron transition between levels represented by two deep-lying terms of the O_I spectrum. This suggests that one or both of the terms $2\,^1\bar{D}$ and $2\,^1S$ may be involved.

In S_I the following terms have been observed :—$3\,^3P$; $(n+1)\,^3S$, $n=3$ to 5; $(n+1)\,^5S$, $n=3$ to 9; $5\,^3P$; $(n+1)\,^5P$, $n=3$ and 4; $(n+1)\,^5D$, $n=3$ to 9; and $3_D\,^3\bar{P}$. In this spectrum also the term system A is fairly complete, with the exception of the $(n+1)\,^3D$ sequence. One of the terms in Table II.—namely, $3_D\,^3\bar{P}$—has been found. Here, again, some unidentified sulphur wave-lengths [1, 3] probably involve terms in the B, C, or D systems.

As Hopfield is continuing his investigations on O_I and S_I, we shall not attempt to extend the analyses of these spectra in this note.

The structure of the spectrum of SeI is not so well known as that of the two former spectra, only the terms $5\,^3S$; $6\,^3P$; $5\,^5P$; $(n+1)\,^5S$, $n=4$ to 10; and $(n+1)\,^5D$, $n=5$ to 11, having been identified. The spectra of Te_I and Po_I have not hitherto been analysed, as far as we are aware.

Some absorption experiments by Zumstein [6] had shown that four wave-lengths of the tellurium arc spectrum were absorbed by tellurium vapour, and some others carried out by Miss Allin in this laboratory that a number of wave-lengths were reversed in the spectrum of an underwater spark between terminals of a Te–Au alloy. With this information before us, we attempted to make an analysis of the Te_I spectrum, and were able to make some progress. Incidentally, as we will show later, we have been able to extend the analysis of the Se_I spectrum.

III. *Results.*

Tellurium I.

In order to aid us in the present investigation, we have re-measured the wave-lengths in the tellurium arc spectrum in the spectral range λ 3200 Å. to λ 1640 Å. The wave-lengths from λ 3200 Å. to 2080 Å. had been observed and measured previously by others, but we believe that our values are more accurate. Those below λ 2080 Å. have been measured for the first time. The wave-lengths with their intensities, frequencies, and the term classification that we have assigned in certain cases are contained in Table III. Three spectrographs were used for the photography of the spectrum, a Hilger E 1 spectrograph of the

Table III.

I.	λ(I.A.).	ν vac.	Classification.
3	3175·15	31485·5	
1	2858·28	34975·8	
6	2769·65	36095·0	$5\,^1\overline{D}_2$—$6\,^3S_1$
6	2530·73	39502·4	$5\,^3P_1$—$6\,^5S_2$
3	2431·71	41110·7	
3	2420·10	41308·0	
17	2385·76	41902·6	$5\,^3P_1$—$6\,^3S_1$
15	2383·24	41946·9	$5\,^3P_0$—$6\,^3S_1$
10	2265·52	44126·3	$5\,^1\overline{D}_2$—a_1
12	2259·02	44253·2	$5\,^3P_2$—$6\,^5S_2$
10	2255·49	44322·5	$5\,^1\overline{D}_2$—b_2
9	2208·74	45260·5	$5\,^1\overline{D}_2$—c_2
8	2159·79	46286·2	
9	2147·19	46557·8	$5\,^1\overline{D}_2$—d_2
20 R	2142·75	46654·2	$5\,^3P_2$—$6\,^3S_1$
12	2081·03	48037·8	$5\,^1\overline{D}_2$—e_2
8	2070·9	48273	$5\,^1\overline{D}_2$—f_3
8	2002·0	49934	$5\,^3P_1$—a_1
6	2000·2	49979	$5\,^3P_0$—a_1
7	1994·2	50130	$5\,^3P_1$—b_2
3	1957·5	51068	$5\,^3P_1$—c_2
4	1957·1	51078	
2	1954·5	51146	
3	1909·1	52363	$5\,^3P_1$—d_2
4	1895·5	52738	
6	1859·9	53751	
8	1856·6	53845	$5\,^3P_1$—e_2
2	1854·3	53906	
6	1853·1	53943	
6	1851·5	53993	
6	1850·0	54037	

TABLE III. (*continued*).

I.	λ(I.A.)). λ (I vac.).	ν vac.	Classification.
3	1844·0	54176	
4	1828·9	54678	$5\,^3P_2—a_1$
6	1825·5	54780	
10	1822·4	54873	$5\,^3P_2—b_2$
3	1798·4	55605	
6	1796·3	55670	
6	1795·7	55689	
2	1791·8	55810	$5\,^3P_2—c_2$
4	1790·7	55844	
3	1777·4	56262	
5	1775·0	56338	
3	1773·8	56376	
5	1759·4	56838	
6	1751·0	57110	$5\,^3P_2—d_2$
3	1733·0	57703	
2	1730·6	57783	
3	1721·2	58099	
3	1712·8	58384	
5	1708·0	58548	
3	1706·7	58593	$5\,^3P_2- e_2$
6	1700·0	58824	$5\,^3P_2—f_3$
5	1688·5	59224	
3	1663·1	60129	
5	1655·4	60408	
3	1645·0	60790	

Littrow type with quartz prism for the range λ 3175 Å. to λ 2081 Å., a Hilger E 31 quartz spectrograph for the range λ 2081 Å. to λ 1856 Å., and a Hilger fluorite vacuum spectrograph for the ultraviolet below λ 1856 Å.

An analysis of the wave-lengths of the tellurium arc spectrum has led to the structure summarised in Table IV. The two wave-lengths λ 2259·02 Å. and λ 2142·75 Å. that we have classified as $5^3P_2—6\,^5S_2$ and $5\,^3P_2—6\,^3S_1$ were observed by Zumstein [6] to be absorbed by tellurium vapour. He also observed in his experiments absorption of λ 2385·76 Å. and λ 2383·24 Å. These we have classified as $5\,^3P_1—6\,^3S_1$ and $5\,^3P_0—6\,^3S_1$ respectively. Kimura[7] recently found that the former pair of wave-lengths involving the term $5\,^3P_2$ were absorbed by normal vapour, while the latter pair were not. This would appear to indicate that λ 2385·76 Å. and λ 2383·24 Å. originate in transitions involving metastable states. Whether or not the term $5\,^3P_0$

Table IV.

Term.		$5\,^1D_2$.	$\Delta\nu$.	$5\,^3P$.	$\Delta\nu$.	$5\,^3P_0$.	$\Delta\nu$.	$5\,P_2$.
	Value.	10,558·6	5807·6	4751·0	44·3	4706·7	4706·7	0
$6\,^5S_2$	44,253·4	—		(6) 2,530·73 39,502·4				(12) 2,259·02 44.253·2
	2,400·2							
$6\,^3S_1$	46,653·6	(6) 2,769·65 36,095·0		(17) 2,385·76 41,902·6		(15) 2,383·24 41,946·9		(20 R) 2,142·7 46,654·2
	8,031·3							
a_1	54,684·9	(10) 2,265·52 44,126·3		(8) 2,002·0 49,934		(6) 2,000·2 49,979		(4) 1,828·9 54,678
	196·2							
b_2	54,881·1	(10) 2,255·49 44,322·5		(7) 1,994·2 50,130				(10) 1,822·4 54,873
	937 8							
c_2	55,818·9	(9) 2,208·74 45,260·5		(3) 1,957·5 51,068				(2) 1,791·8 55,810
	1,297·5							
d_2	57,116·4	(9) 2,147·19 46,557·8		(3) 1,909·1 52,363				(6) 1,751·0 57,110
	1,480·0							
e_2	58,596·4	(12) 2,081·03 48·037·8		(8) 1,856·6 53,845				(3) 1,706·7 58,593
	236							
f_3	58,832	(8) 2,070·9 48,273						(6) 1,700·0 58,824

in Table IV. is valid or not is uncertain. The negative difference $5\,^3P_0 - 5\,^3P_1 = -44{\cdot}3$ is rather unusual and only occurs twice, but we have not been able to bring the strong line λ 2383·24 Å. in any other way into the structure of the spectrum. The fact that singlet-quintet intercombination lines are rarely observed explains the absence of $5\,^1D_2 - 6\,^5S_2$.

We have not been able to identify definitely any of the terms of higher energy than $6\,^3S_1$, because the estimated intensities of the wave-lengths that involve these terms are of little use as a guide in selecting multiplets. This is on account of the fact that the wave-lengths are spread over such a large spectral range. We have therefore designated the terms that we have worked out by small letters *a*, *b*, *c*, etc., with the inner quantum numbers that our analysis has has led us to inscribe as subscripts.

Selenium I.

In our investigation of the tellurium arc spectrum we observed five wave-lengths in it that were due to the presence of selenium as an impurity in the tellurium metal we used for arc terminals. We have found that these five wave-lengths are the most fundamental ones of the Se_I. spectrum, and have classified them in the first two rows of Table V. Our classification has been strongly supported by the observation made by Kimura [7] that the four more intense of these five wave-lengths were reversed in a selenium arc.

Another multiplet—namely, that classified as $4\,^3P - 5\,^3D$—is included in the table. The wave-lengths in this multiplet were obtained from tables of measurements by McLennan, Young, and Ireton [8]. The frequency differences, however, are not very exact, so that the correctness of the classification is rather doubtful.

Conclusion.

The addition that we have been able to make to the known structure of the Se I. spectrum and our analysis of the Te I. spectrum have shown that, in so far as they are known, these spectra are similar to those of O_I and S_I. All four spectra have been shown to conform to the theoretical structures predicted for them by the Pauli-Heisenberg-Hund theory. The structure for Po_I is not yet known, as only a very few wave-lengths that belong to its arc spectrum have been observed.

TABLE V.

Term.		$4\,^3P_0$.	$\Delta\nu$.	$4\,^3P_1$.	$\Delta\nu$.	$4\,^3P_2$.
	Value.	2,534	544	1,990	1,990	0
$5\,^5S_2$	48,187			(1) 2,164·0 46,196		(3) 2,074·6 48.187
$\Delta\nu$	2,814					
$5\,^3S_1$	51,001	(8) 2,062·6 48,467		(10) 2,039·7 49,011		(10) 1,960·2 51,000
$\Delta\nu$	10,687					
$5\,^3D_1$	61,688	(3) 1,690·4 59,158		(3) 1,674·9 59,705		(2) 1,621·3 61,679
$\Delta\nu$	148					
$5\,^3D_2$	61,836			(4) 1,670·8 59,852		(1) 1,617·3 61,831
$\Delta\nu$	407					
$5\,^3D_3$	62,243					(2) 1,606·6 62,243

The authors wish to take this opportunity to thank Mr. Crawford and Mr. Clark, who assisted us greatly by photographing the tellurium arc spectrum in the extreme ultra-violet region with the fluorite vacuum spectrograph. To Miss Allin our thanks are also due for contributing the results of her investigations on the under-water spark spectrum of tellurium. Finally, acknowledgment should be made to the National Research Council of Canada for the award of a studentship to one of us, Mr. J. H. McLeod, that made it possible for him to take part in this investigation.

References.

1. Fowler, 'Series Spectra,' 1922.
2. Hopfield, Astr. Journ. lix. p. 114 (1924); Phys. Rev. xxix. 6, p. 923 (1927).
3. Hopfield, 'Nature,' cxii. p. 437 (1923).
   Hopfield and Birge, 'Nature,' cxii. p. 790 (1923).
   Laporte, *Naturwiss.* xii. p. 598 (1924).
4. Birge, J. O. S. A. viii. p. 233 (1924).
5. Bungartz, *Ann. der Phys.* lxxvi. p. 709 (1925).
   Hopfield and Dieke, Phys. Rev. xxvi. 5, p. 638 (1926).
6. Zumstein, Phys. Rev. xxvii. 5, p. 562 (1926).
7. Kimura, Jap. Journ. of Phys. iv. 2, p. 81 (1926-27).
8. McLennan, Young, and Ireton, Proc. Roy. Soc. A, xcviii. p. 95 (1920).

XLV. *Application of Schrödinger's Wave Functions to the Calculation of Transition Probabilities for the Principal Series of Sodium.* By Y. Sugiura *.

Introduction.

Hoyt †, Thomas ‡, and Bartels § have tried to calculate the transition probabilities of the series electrons in sodium by the application of the correspondence principle to the orbital model of the sodium atom. In all calculations of this kind only an estimate of the transition probabilities could be obtained, due to the lack of a rational method of averaging between initial and final orbits. The recent development of quantum mechanics of Heisenberg ‖ and Schrödinger ¶ has removed this difficulty, so that it is now possible to calculate rationally the transition probabilities of the series electron not only in hydrogen, but also in higher atoms, as soon as the expression for the potential energy is known.

The rigorous quantum mechanical solution of the problem of an atom with several electrons involves very difficult calculations, but for many purposes a satisfactory treatment may be based on a comparison of the behaviour of the elements with that to be expected from the stationary states of an electron moving in a central field of force. As regards

* Communicated by Prof. N. Bohr, Ph.D.

† F. C. Hoyt, Phil. Mag. xlvi. p. 135 (1923); Phys. Rev. xxv. p. 174; xxvi. p. 749 (1925).

‡ W. Thomas, *Zs. f. Phys.* xxiv. p. 169 (1924).

§ H. Bartels, *Zs. f. Phys.* xxxii. p. 415 (1925).

‖ W. Heisenberg, *Zs. f. Phys.* xxxiii. p. 879 (1925), and various papers in *Zs. f. Phys.*

¶ E. Schrödinger, *Ann. d. Phys.* lxxix. p. 361 (1926), and four other papers by the same author in *Ann. d. Phys.*

the latter problem Kramers * has shown quite recently that a rational first approximation to the quantum-mechanical calculation may be obtained by using an orbital model fixed by the usual quantum conditions, if in these half-number values are introduced for the radial and azimuthal quantum numbers. As already shown in a paper by Urey and the writer †, it is in fact possible in case of the X-ray spectra of the heavier elements to construct an interatomic field which allows us to account closely for the observed X-ray terms by means of these conditions.

Relying on the same method of approximation and applying Schrödinger's theory of wave functions, it is attempted in the present paper to calculate the transition probabilities for the principal series of the optical spectrum of sodium. Compared with the problem treated in the previous paper the present problem presents the simplicity that in constructing the central field we may neglect the effects of the spin of the electron and relativity modifications of mechanics. In fact, for the optical terms as well as for the X-ray terms, the doublets arising from these effects are quite small compared with the possible errors involved in our calculation.

§ 1. *Central Field in Sodium Atom.*

In Table I. are given the values of the spectral terms taking the Rydberg constant R as unity. The term values are compiled from the well-known reports of Siegbahn and Fowler and are denoted in the usual way by the symbol n_k. The field corresponding to these terms is derived by means of the quantum condition ‡

$$n-k+\tfrac{1}{2} = \frac{\sqrt{2}}{\pi}\log_e 10 \times \int_{10^x\,\text{min.}}^{10^x\,\text{max.}} \sqrt{-\frac{1}{2}\left(\frac{\nu}{\mathrm{R}}\right)10^{2x}-\tfrac{1}{2}(k-\tfrac{1}{2})^2+\mathrm{Q}}\,dx, \quad (1)$$

where for the sake of convenience a logarithmic scale for the radius vector r is used,

$$x = \log_{10}\frac{r}{a_{\mathrm{H}}} \quad \text{and} \quad a_{\mathrm{H}} = \frac{h^2}{4\pi^2 me^2},$$

* H. A. Kramers, *Zs. f. Phys.* xxxix. p. 828 (1926).

† Y. Sugiura and H. Urey, Communication Copenhagen Academy, *Math.-fys.* vii. p. 13 (1926).

‡ Comp. Sugiura and Urey, *l. c.*

a_H being half the major axis of the electron orbit in the orbital model of the normal state of the hydrogen atom. Further,

$$Q = \frac{r^2}{e^2 a_H} V,$$

where V is the potential energy of the electron in the central field. In order to evaluate Q as a function of x we draw in a Q, x diagram first the curve 10^{2x} and cut the paper along this curve, so that by sliding along the x- and Q-axis by amounts equal to $\frac{1}{2}\left(\frac{\nu}{R}\right)$ and $\frac{1}{2}(k-\frac{1}{2})^2$ respectively, we can draw the Q-curve to fit the condition (1) for all n_k terms as closely as possible. The Q-curve thus obtained is shown in the accompanying figure and the accuracy of the computation is illustrated by the last column of Table I. obtained by introducing the function Q given by this curve in (1).

TABLE I.

n_k.	$\left(\frac{\nu}{R}\right)$ obs.	$(n-k)$ calc.
1_1	78·8	0 00
2_1	4·33	1·01
2_2	2·08	0·00
3_1	0·378	2·02
3_2	0·223	1·00
3_3	0·112	0·00
4_1	0·143	3·03
4_2	0·101	1·99
4_3	0·0629	1·00
4_4	0·0625	0·00
5_1	0·0752	4·02
5_2	0·0584	2·98
5_3	0·0402	1·99
5_4	0·0400	0·99
6_1	0·0463	5·02
6_2	0·0378	3·96
6_3	0·0279	2·98
6_4	0·0277	1·98

§2. *Schrödinger's Proper Functions for* 3_1, 3_2, *and* 4_2 *Orbits of Sodium.*

In the case of a central field, we have the following expression for Schrödinger's wave equation:

$$\rho^2\frac{d^2\chi_{n,k}}{d\rho^2}+2\rho\frac{d\chi_{n,k}}{d\rho}-\left\{\underset{\mathrm{R}}{\nu_{n,k}}\rho^2-2\mathrm{Q}+k(k-1)\right\}\chi_{n,k}=0,$$

$$k=1,\ 2,\ 3\ \ldots,$$

where $\chi_{n,k}$ is a function of ρ only, ρ being $\frac{r}{a_{\mathrm{H}}}$ and Schrödinger's proper function

$$\Psi_{n,k,m}=\chi_{n,k}(\rho)\mathrm{F}_{k,m}(\theta,\phi)$$

for polar coordinates ρ, θ, ϕ. If we can regard a small portion of Q as a part of a parabola, the above differential equation may be written generally as follows:

$$\frac{d^2\mathrm{R}_{n,k}}{d\rho^2}+\left(\mathrm{A}+\frac{\mathrm{B}}{\rho}+\frac{\mathrm{C}}{\rho^2}\right)\mathrm{R}_{n,k}=0,$$

where $\mathrm{R}_{n,k}=\rho\chi_{n,k}$.

Putting

$$x=2\sqrt{-\mathrm{A}}\,\rho,$$

we have

$$\frac{d^2\mathrm{R}_{n,k}}{dx^2}+\left(-\tfrac{1}{4}+\frac{\kappa}{x}+\frac{\frac{1}{4}-\mu^2}{x^2}\right)\mathrm{R}_{n,k}=0,$$

where $\kappa=\dfrac{\mathrm{B}}{2\sqrt{-\mathrm{A}}}$ and $\mu^2=\frac{1}{4}-\mathrm{C}$.

The solution of this differential equation can be expressed in terms of confluent hypergeometric functions $\mathrm{M}_{\kappa,\pm\mu}$* and

$$\mathrm{R}_{n,k}=\mathrm{C}_1\mathrm{M}_{\kappa,\mu}+\mathrm{C}_2\mathrm{M}_{\kappa,-\mu},\quad\ldots\quad(2)$$

where

$$\mathrm{M}_{\kappa,\pm\mu}=e^{-\frac{1}{2}x}x^{\frac{1}{2}\pm\mu}\left\{1+\frac{\frac{1}{2}\pm\mu-\kappa}{1!\,(1\pm2\mu)}x+\frac{(\frac{1}{2}\pm\mu-\kappa)(\frac{3}{2}\pm\mu-\kappa)}{2!\,(1\pm2\mu)(2\pm2\mu)}x^2+\ldots\right\},$$

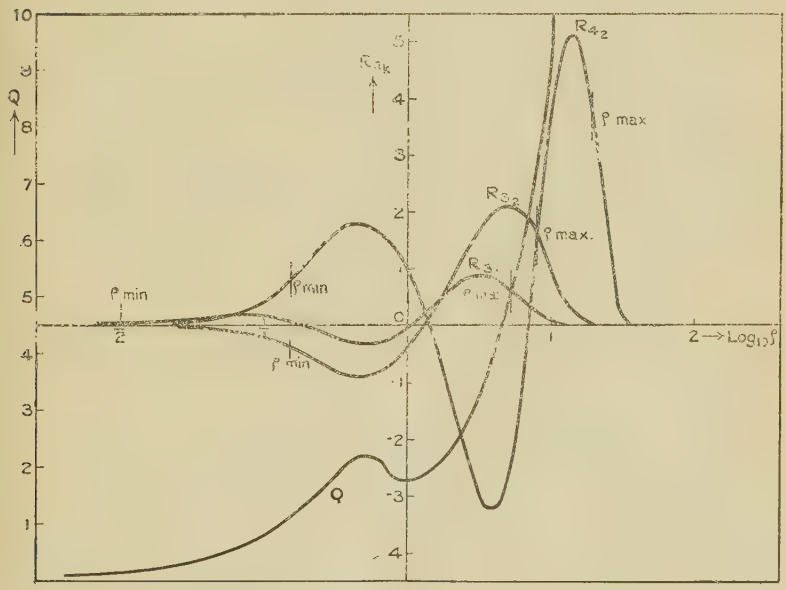
if 2μ is not an integer. For large values of $|x|$ we have generally two asymptotic expressions, one of which is Whittaker's

$$\mathrm{W}_{\kappa,\mu}\sim e^{-\frac{1}{2}x}x^{\kappa}\times\left[1+\sum_{j=1}^{\infty}\frac{\{\mu^2-(\kappa-\frac{1}{2})^2\}\{\mu^2-(\kappa-\frac{3}{2})^2\}\ldots\{\mu^2-(\kappa-j+\frac{1}{2})^2\}}{j!\;x^j}\right],\quad\ldots\quad(3)$$

* Whittaker and Watson, 'Modern Analysis,' Chap. xvi. p. 337.

while we cannot use the other expression, since it becomes infinity at x=infinity and does not satisfy the boundary condition.

We start to calculate the function $R_{n,k}$ from infinity where the field is determined by Coulomb's law, using the expression (3). At the point where two consecutive different expressions of Q meet, our function $R_{n,k}$ has to satisfy the two conditions: $R_{n,k}$ and $\frac{dR_{n,k}}{d\rho}$ shall have the same value on both sides of the point. By these two conditions we can determine the constants C_1 and C_2 in the expression (2) at



Q: Field curve.
$R_{n,k}$: Schrödinger's proper function of the n_k state.

the one side of every connecting point, if they are known on the other side. We pass, in this way, from infinity to the other boundary at zero and test if the boundary condition at zero is satisfied or not. If the field expression and the term value were not correct, we could not obtain a function $R_{n.k}$ which satisfied all the conditions. We tried to modify the field expression, until we obtained functions $R_{n,k}$ which satisfied the boundary conditions. A slight modification of the field Q in the part, where Q was obtained graphically by (1), was sufficient to give the functions $R_{n,k}$ for the 3_1, 3_2

and 4_2 states, which satisfied all conditions. R_{3_1} cuts the zero line twice and the tangent at zero is not zero, while R_{3_2} and R_{4_2} cut the zero line once and twice respectively and then tangent at zero is zero, as is to be expected. The curvature of $R_{n,k}$ between extreme radii of the corresponding orbit is positive, while outside of them it is negative as shown in the figure.

§ 3. *Transition Probabilities for the Principal Series of Sodium.*

As is well known, the spectra of sodium and hydrogen are doublet spectra. We are interested, however, only in the whole intensity of the two components of a doublet, since we can easily determine the relative intensities of the components by the statistic weights of the stationary states. Taking, therefore, the case of a central field, where the doublet system is neglected, the part $F_{k,m}(\theta, \phi)$ of Schrödinger's function $\Psi_{n,k,m}$ which depends upon the angles is the same as in the case of hydrogen, in which the spinning electron effect is neglected :

$$\Psi_{n,k,\pm m} = \chi_{n,k}(\rho)\, F_{k,m}(\theta, \phi)$$

$$= \frac{R_{n,k}(\rho)}{\rho} P_{k-1,m}(\cos\theta) \begin{matrix}\cos \\ \sin\end{matrix} m\phi,$$

where $P_{k-1,m}(\cos\theta)$ is the associated Legendre function of the $(k-1)$th degree and mth order.

We can now express Heisenberg's matrix coordinates X, Y, Z by Schrödinger's proper functions as follows :—

$$\left.\begin{matrix}X\\Y\\Z\end{matrix}\right\}_{n,k,m;\,n',k',m'} = \int \begin{matrix}x\\y\\z\end{matrix} \Psi_{n,k,m}\, \overline{\Psi}_{n',k',m'}\, d\Omega,$$

$$d\Omega = r^2 \sin\theta\, dr\, d\theta\, d\phi,$$

where the integration is to be extended over the whole space. In our special case of the principal series of sodium, leaving apart the doublet system, we have the following three possible cases :—(I.) n, 2, $-1 \to 3$, 1, 0 ; (II.) n, 2, $0 \to 3$, 1, 0 ; (III.) n, 2, $1 \to 3$, 1, 0 for $n, k, m \to n', k', m'$. The probabilities of these three transitions are equal ; the angular part of the proper functions gives therefore a factor $\frac{1}{3}$ in the square of the amplitudes for each of these transitions. The normalised square of amplitude in the sense of quantum

mechanics, corresponding to the sum of all possible cases, is then given by

$$\sum_{(I)(II)(III)} (X^2+Y^2+Z^2)_{n_2,\,3_1} = a_H{}^2 \frac{\left(\int_0^\infty \rho R_{n_2} R_{3_1}\, d\rho\right)^2}{\int_0^\infty R_{n_2}{}^2\, d\rho \int_0^\infty R_{3_1}{}^2\, d\rho} \qquad (4)$$

which can be calculated graphically by a planimeter, since R_{n_2} and R_{3_1} are known in the whole region of ρ.

On the other hand, the total energy radiated per unit time from one atom is classically

$$-\frac{dE}{dt} = \frac{2}{3c^3} \Sigma\, \overline{\ddot{\mathfrak{P}}^2} = \Sigma \frac{(2\pi\nu)^4}{3c^3} \overline{\mathfrak{P}^2}, \quad . \quad . \quad . \quad (5)$$

corresponding to linear oscillators with moments

$$\mathfrak{P} = p \cos 2\pi\nu\tau t,$$

where p is *charge* times *classical amplitude*. By the definitions of the classical and the matrix amplitude, we have for a definite state n as a classical expression of amplitude

$$\mathbf{A}_n = \sum_\tau C_\tau \cos 2\pi(\tau\nu t + \delta_\tau),$$

which is to be compared with the matrix expression *

$$\mathbf{A}_n = \mathbf{A}_{nn} + \sum_m \left(\mathbf{A}_{nm}\, e^{2\pi i \nu_{nm} t} + \mathbf{A}_{mn}\, e^{2\pi i \nu_{mn} t}\right),$$

or $C_\tau \cos 2\pi(\tau\nu t + \delta_\tau)$ corresponds to $\mathbf{A}_{nm}\, e^{2\pi i \nu_{nm} t} + \mathbf{A}_{mn}\, e^{2\pi i \nu_{mn} t}$. When we take the time mean value of the square of amplitude,

$$\tfrac{1}{2} C_\tau{}^2 \text{ corresponds to } 2\mathbf{A}_{nm}\mathbf{A}_{mn}, \quad . \quad . \quad . \quad (6)$$

so that a factor 4 appears in the quantum mechanical expression for the square of amplitude corresponding to the transition between two states.

According to Einstein's conception of spontaneous transition $P \to Q$,

$$-\frac{dE}{dt} = \sum_Q A_{PQ}\, h\nu_{PQ}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and the transition probability $\sum_Q A_{PQ}$ for all possible transitions $P \to Q$ is given generally by

$$\sum_Q A_{PQ} = \frac{1}{g_P} \sum_{P,\,Q} A_{PQ}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

* O. Klein, *Zs. f. Phys.* xli. p. 433 (1927).

while the number of dispersion electrons f is defined by

$$3f = \tau_\nu \sum_{\mathrm{P}} \mathrm{A_{QP}} = \tau_\nu \frac{1}{g_\mathrm{Q}} \sum_{\mathrm{P,Q}} \mathrm{A_{QP}}, \quad . \quad . \quad . \quad (9)$$

where $\tau_\nu = \dfrac{3mc^3}{8\pi^2 e^2 \nu^2}$; g_P and g_Q are the statistic weights of P and Q states. From (8) and (9) we have Ladenburg's relation *

$$3f = \tau_\nu \frac{g_\mathrm{P}}{g_\mathrm{Q}} \sum_{\mathrm{Q}} \mathrm{A_{PQ}}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Equating (5) and (7) and taking (4) and (6) into account, the transition probability expressed by Schrödinger's proper functions is

$$\sum_{\mathrm{Q}} \mathrm{A_{PQ}} = \frac{1}{g_\mathrm{P}} \frac{4(2\pi\nu)^4 e^2}{3hc^3\nu} a_\mathrm{H}^2 \frac{\left(\int_0^\infty \rho \mathrm{R_P R_Q}\, d\rho\right)^2}{\int_0^\infty \mathrm{R_P}^2\, d\rho \int_0^\infty \mathrm{R_Q}^2\, d\rho}$$

$$= \frac{1}{g_\mathrm{P}} 2{\cdot}682 \,.\, 10^9 \,.\, \left(\frac{\nu}{\mathrm{R}}\right)^3 \frac{\left(\int_0^\infty \rho \mathrm{R_P R_Q}\, d\rho\right)^2}{\int_0^\infty \mathrm{R_P}^2\, d\rho \int_0^\infty \mathrm{R_Q}^2\, d\rho}, \quad (11)$$

because in our case all ν_{PQ} are nearly the same ν. Putting (11) in (10) we have

$$3f_{\mathrm{PQ}} = \frac{1}{g_\mathrm{Q}} \left(\frac{\nu}{\mathrm{R}}\right) \frac{\left(\int_0^\infty \rho \mathrm{R_P R_Q}\, d\rho\right)^2}{\int_0^\infty \mathrm{R_P}^2\, d\rho \int_0^\infty \mathrm{R_Q}^2\, d\rho} \quad . \quad . \quad . \quad (12)$$

In our special case of the principal series of sodium $g_\mathrm{P}=3$ and $g_\mathrm{Q}=1$. Using the expressions (11) and (12), we can calculate the transition probability and the number of dispersion electrons for each line of the principal series of sodium, which are shown in the following table.

TABLE II.

n_2–3_1.	$\dfrac{\nu}{\mathrm{R}}$.	$\dfrac{1}{a_\mathrm{H}^2} \Sigma (\mathrm{X}^2+\mathrm{Y}^2+\mathrm{Z}^2)_{n_2, 3_1}$.	$\mathrm{A}_{n_2, 3_1}$ (in sec^{-1}).	f.	
3_2–3_1	·1545	18·89	·6228 10^8	·9728	
4_2–3_1	·2770	·1562	·0297	·0144	
5_2–3_1	·3193	.....	·0152	·0056	Estimated.
6_2–3_1	·3398	.....	·00878	·0028	Estimated.
7_2–3_1	·3511	.....	·00553	·0017	Estimated.
8_2–3_1	·3580	.....	·00371	·0011	Estimated.

* R. Ladenburg, *Zs. f. Phys.* iv. p. 451 (1921).

The values of $A_{n_2, 3_1}$ for higher members than 5_2–3_1 are estimated by assuming the law $A_{n,k\,:\,n',k'} \infty \frac{1}{n^3}$, which is proved theoretically for large values of n in the case of hydrogen, and verified by Trumpy * experimentally in the case of sodium. From the values of $A_{n_2, 3_1}$, we can compute those of f by the expression (10). The transition probability for each D-line of sodium, deduced from the experimental results of Minkowski †, is $0{\cdot}64 \,.\, 10^8$ sec^{-1}, which is only a little larger than the computed value $0{\cdot}62 \,.\, 10^8$ sec^{-1}. According to Kuhn ‡ and Thomas §, the sum of dispersion electrons for all principal series lines and the continuous absorption should be unity in the one electron problem, and this is, moreover, one of the most important relations in the quantum mechanics. In the case of the sodium atom, the total sum of dispersion electrons ought not, in reality, to be unity, but it is nearly one. When we assume, as in the present calculation, the central field and replace the actual problem of many electrons by one electron problem, we should have one for the value of the total sum of dispersion electrons, as the consequence of the quantum mechanics. In order to get the total sum of the dispersion electrons in our special case, however, we have still to take into account the transition 3_1–2_2, which is impossible in the actual state of sodium. By a similar method as for 3_1, 3_2, and 4_2 states, we can get the wave function for 2_2 state, which gives for the value of the square of matrix amplitude

$$\frac{1}{a_H{}^2}\Sigma(X^2+Y^2+Z^2) = \frac{\left(\int_0^\infty \rho R_{2_2} R_{3_1}\, d\rho\right)^2}{\int_0^\infty R_{2_2}{}^2\, d\rho \int_0^\infty R_{3_1}{}^2\, d\rho} = 0{\cdot}0752.$$

Knowing $\left(\frac{\nu}{R}\right)_{3_1, 2_2} = 1{\cdot}70$, we obtain the contribution in the number of dispersion electrons due to the transition 3_1—2_2: $f_{3_1, 2_2} = 0{\cdot}043$, which is to be subtracted from $\sum_{n=3}^{\infty} f_{n_2, 3_1} + f$ (continuous). On the other hand, we find $\sum_{n=3}^{8} f = 0{\cdot}998$, so that $\sum_{n=2}^{8} f = 0{\cdot}955$, to which we have still

* B. Trumpy, *Zs. f. Phys.* xxxiv. p. 715 (1925).
† R. Minkowski, *Zs. f. Phys.* xxxvi. p. 839 (1926).
‡ W. Kuhn, *Zs. f. Phys.* xxxiii. p. 408 (1925).
§ W. Thomas, *Naturwissenschaften*, xiii. p. 627 (1925).

to add some contribution due to higher members of the series and due to the continuous absorption. Since this total sum should be unity our calculation shows that the contribution in f due to the continuous absorption is about 0·04.

Conclusion.

In conformity with the result of Kramers, mentioned in the introduction, we have in this paper found the proper functions in the sense of Schrödinger belonging to 3_1, 3_2, and 4_2 states of the sodium atom from the observed term values and the central field obtained by a calculation based on an orbital conception. In this way we could avoid the laborious calculations, which are necessary when the solution of the problem in question is required immediately from the solution of a wave equation. The proper functions thus obtained were then used for the calculation of the transition probabilities and the number of dispersion electrons for the principal series of sodium.

According to Minkowski, as stated above, the transition probability for the D-line $0{\cdot}64 \cdot 10^8\,\mathrm{sec}^{-1}$ gives already $f_{D_1+D_2} \simeq 1$ (f = number of dispersion electrons), which seemed to be too big, since even in the case of sodium $\Sigma f \simeq 1$. From our calculations, which give a very rapid decrease of f from the first to the higher members of the principal series in sodium, we can, however, see that Minkowski's result is quite reasonable from the point of view of Kuhn's and Thomas' argument.

Finally, the author wishes to express his best thanks to Professor N. Bohr, Dr. W. Heisenberg, and Dr. O. Klein for their kind interest and valuable advice in the present calculation. Especially he wishes to express his sincere thanks to Professor H. A. Kramers who suggested it to him to carry out this work.

Universitetets Institut for teoretisk Fysik,
København.

XLVI. *Ionization by Collision and a "Photoelectric Theory" of the Sparking Potentials. A Reply to Mr. Huxley.* By James Taylor, *M.Sc., Ph.D., A.Inst.P.*; *The Physical Institute of the University of Utrecht* *.

In a recent communication to this Journal H. G. L. Huxley (Phil. Mag. May 1927) has considered a Theory of the Sparking Potentials recently put forward by the present writer (James Taylor, Proc. Roy. Soc. A. vol. cxiv. p. 73, 1927; Phil. Mag. iii. p. 753, 1927). In contradistinction to Townsend's Theory we shall refer to this new hypothesis as the "Photoelectric Theory" of the Sparking Potentials. Huxley brings forward a number of objections to the Photoelectric Theory and concludes that it cannot be satisfactory. The object of the present paper is therefore to consider the objections raised, and at the same time give some account of the circumstances which brought about the enunciation of the theory.

The usual accepted Theory of the Sparking Potentials is that of Townsend "which is based upon his theory of ionization by collision in which both electrons and positive ions are assumed to produce new ions by collision with the molecules of the gas in cases where the pressure is large and the sparking potential is above the minimum."

The Townsend theory of ionization by collision for negative ions or electrons is not universally adopted, but leaving this aside, the objections that can be raised against the Townsend Sparking Potential Theory are :—

(1) The hypothesis that low-speed positive ions produce new ions by collision with the molecules of the gas in which they are moving is open to doubt.

(2) According to this Theory, the sparking potentials should be independent of the nature and condition of the cathode surface, whilst in practice it is found to be largely dependent upon these.

The question (1) of the production of ionization and electrons by the action of low-speed positive ions is one which has called forth much controversy. In some recent work "On the Electric Discharge through Gases at very low pressures," Sir J. J. Thomson (Phil. Mag. xlviii. p. 1, 1924) deals somewhat extensively with the question of ionization by collision of positive ions, and raises several objections to the hypothesis that low-speed positive ions are

* Communicated by Prof. L. S. Ornstein.

able to ionize by collision against gas molecules. He discusses other methods by which the ionization in the discharge (often attributed to the above action) may be produced, and puts forward an alternative and very interesting hypothesis according to which the positive ions liberate photoelectrons by the action of the radiation emitted when they are neutralized at the cathode surface. A later paper gives experimental verification of such an action (Sir J. J. Thomson, Phil. Mag. ii. p. 675, 1926).

The photoelectric theory of the sparking potentials arose naturally out of the above hypothesis of Sir J. J. Thomson. It was also an expression of the conviction, derived from a study of the Schumann radiations of the electric discharge in rare gases, that it is necessary to attribute a not unimportant part of the mechanism of the discharge to the radiations given out by the gas.

With regard to (2) it has been shown by numerous experimenters that the nature and condition of the electrodes have a very considerable effect upon the value of the sparking potentials obtained (*cp.* Holst and Oosterhuis, Phil. Mag. xlvi. p. 1117, 1923 ; Taylor, *loc. cit.*). and that the changes from metal to metal are as large as those from gas to gas. Townsend's Theory, in its unmodified form, fails entirely to account for such changes, and they have often been attributed to impurities in the gas (except for the alkali and alkali earth metals). To test this, the writer carried out experiments in which the conditions were very carefully chosen. The results showed that, with an identical filling gas, changes of the sparking potential (with nickel electrodes) of as much as 65 volts in 170 volts could be brought about by alteration of the cathode surface (Taylor, Phil. Mag. iii. p. 762, 1927). Polarization effects in which temporary changes of the sparking potentials were exhibited (Phil. Mag. iii. p. 755, 1927) due to change in the electrode surface conditions were also observed. Later work (Proc. Roy. Soc. *loc. cit.*) in which carefully purified argon was used, and in which the electrodes were formed by evaporation of tungsten in vacuum, and were perhaps purer than any electrodes previously used in sparking potential work, showed that the sparking potential was a function of the nature and condition of the cathode surface and varied continuously with changes of the latter. Results with "sodiumated" electrodes (formed by electrolysis through the glass walls of the discharge-tubes) further supported this view.

Any satisfactory theory of the sparking potentials must then be able to account for such important electrode surface

effects. The Townsend theory fails to do this. On the other hand, the photoelectric theory gives a satisfactory explanation.

To proceed to the objections raised by Huxley. The writer was aware of the difficulties in question (see Townsend, Phil. Mag. xlv. p. 44, 1923), and refers to them in one of the papers (Phil. Mag. iii. p. 766, 1927) in the following words:—"Nevertheless there are still difficulties in the light of certain experimental evidence in accepting such a theory as outlined above; it is hoped, however, to continue work in this direction, and a fuller consideration of the theory will be given in a later paper." It was pointed out that experiments were in progress in which both the photoelectric emissivity γ (for the actual radiation emitted by the gas) and the sparking potential v_c were being measured, and it is on this definite experimental control which is being carried out at the present time, that the writer looked to and still looks to giving a conclusive answer as to the value of the hypothesis.

At the same time it is wise to discuss the points raised by Huxley. In paragraph (3) of his paper the discharge between a wire and coaxial cylinder is considered. It is stated that "it is found that the critical force X_1, at the surface of the wire necessary to initiate the discharge, is independent of the diameter of the outer cylinder provided the latter exceeds a certain value. Experimenters who have studied these phenomena are in general agreement on this point." In the opinion of the present writer the experiments on which this generalization is based have been performed only over a very limited range of conditions. Nevertheless the conclusion may be accepted as approximately correct, and Huxley deduces from it rightly that the function γ, in the writer's hypothesis, should be independent of the force at the negative electrode for this case. (This does not imply, however, that γ is independent of the pressure of the gas.)

In Table (I.) are given some results of Watson quoted by Townsend (*Handbuch der Radiologie*, i., Leipzig, 1920) in connexion with the above generalization relative to the electric force X_1, at the surface of the wire. When we consider the electric force X at the surface of the outer cylinder it is seen that X/P is of the order of one volt per cm. per mm. The gas for the case considered is air. In the second Table the value of $X/P \left(= \frac{X_c}{P} \right)$ is about 40 volts per cm. per mm. pressure.

TABLE (I.).

E. A. Watson, 'The Electrician,' vol. xi. Feb. 1910.

Cylinder and wire. Air.

Pressure P. mm.	Diameter wire $2a$.	X_1. Kilovolts per cm.	X. Kilovolts per cm.	X/P. Volts.
760	0·1	75	0·37	0·5
560	0·136	55	0·37	0·67
360	0·211	34	0·36	1·0
760	0·2	61	0·61	0·8
560	0·27	44·5	0·6	1·08
360	0·42	28·5	0·6	1·67
760	0·5	46·5	1·16	1·52
560	0·68	35·0	1·19	2·12
360	1·055	22·0	1·16	3·22

In above outer cylinder diameter=20 cm.

TABLE (II.).

P. mm.	Diameter wire, $2a$. cm.	C. cm.	X_1. Kilovolts per cm.	X_c. Kilovolts per cm.	X_c/P. volts.
760	1·0	0·66	40·0	30·3	40
360	1·0	0·82	23·0	14·0	39
108	1·0	1·12	9·45	4·21	39
25·2	1·0	1·73	3·4	0·98	39

C is the least value of the radius of the outer cylinder for which the condition relative to the critical field holds.

X_c is the field at the surface of the cylinder of radius c cm.

Huxley then considers the sparking potential for parallel plate electrodes, and concludes that in this case there is a large variation of γ with the value of X. This appears to be contradictory to the conclusion, arrived at for the case of cylindrical electrodes, that γ was constant. It is, however, not necessarily the case. We see, from the table given by Huxley, for air, that X/P for the cases considered is between 131 and 440 volts per cm. per mm. In the previous case we saw that this value was of the order of some volts. The experimental evidence is not large, and it was for this reason that the writer avoided such controversial points in the previous papers, hoping rather to control the hypothesis by definite experiment than by plausible considerations. Nevertheless, these differences of X/P for the two cases are striking ; and it would appear that the velocity with which the positive ions impinge upon the cathode is much greater for the case of the plane electrodes than for the cylindrical

ones considered. We are thus led to infer that γ (for a given pressure) may be constant provided the field at the surface of the cathode is not above a certain value, or, in other words, provided that the positive ions do not strike against the electrode with too large a velocity. Also it can be assumed that as the velocity of the positive ions increases, so does the function γ.

This effect of increased electronic emission produced by positive ions bombarding a metal target with positive ions of increasing velocity has been recently considered (see for example, Jackson, Phys. Rev. xxviii. 3, p. 526, 1926), and it has been shown that the number of electrons grows as the speed of the impinging positive ions is increased. We may imagine then that provided the velocity of the positive ion is sufficiently small the photoelectric effect is simply due to the single neutralization of the ion, but when the velocity is sufficiently increased (due to increase of the surface field), we may consider with Sir J. J. Thomson (Phil. Mag. *loc. cit.*) that

"A positive ion striking against the cathode may alternate from the charged to the uncharged condition, if it has much energy, many times before it loses its charge for the last time ; each change from the charged to the uncharged state would be accompanied by the emission of radiation." This action would evidently bring about an increase of γ with the electric field X.

It is further stated that the writer's hypothesis is unable to explain the large difference between the force at the surface of a wire, required to start a negative and a positive discharge. This statement cannot be accepted. The electric field at the cathode is entirely different in the two cases, and the circumstances of the genesis of the electrons from the cathode and the magnification by collision both lead to a difference of field in the required direction.

It may further be pointed out that Huxley's criticisms for the most part imply the acceptance of Townsend's theory of ionization by collision for electrons. In the writer's work the photoelectric hypothesis was fitted into the existing fabric merely as an example of its application, but nowhere was a belief of the authenticity of Townsend's theory of ionization put forward, for this is quite unnecessary from the point of view of the photoelectric hypothesis. In the same way it was suggested that the hypothesis could be fitted into the theory of Holst and Oosterhuis. (These physicists simply maintain a different hypothesis of the production of electrons from the cathode.)

Huxley is correct in his statement therefore (paragraph (4)): "It is no argument therefore in favour of Taylor's hypothesis to be able to state that it can be fitted into the relation obtained by Holst and Oosterhuis." On the other hand, it is no argument in favour of the Townsend Theory.

Turning now to paragraph (5) of Huxley's paper. In this part Dubois' results are mentioned and apparently assumed to be in contradiction to those of the present writer. This is most difficult to understand. If we do assume that Dubois' results are due to saline impurities on the electrodes, it is necessary to give some explanation of their action. An unmodified Townsend Theory fails entirely to give such an explanation, indeed it implies that they are without action at all. On the other hand, if the effect is due "to the action of positive ions in causing electrons to be set free, by bombardment, from impurities on the surface," then we are immediately introducing a foreign hypothesis on top of the original one; and since ordinary electrodes exhibit large variations in the value of the sparking potentials, the effect attributed to the new action becomes of large importance, and the Townsend Theory must be modified to account for it.

Now, it is well known that alkali metal impurities very considerably increase the photoelectric emissivity of a metal surface, and this suggests that the correct explanation is afforded by the Photoelectric Sparking Potential Theory.

"Dubois' conclusions indicate, therefore, that with ordinary metal electrodes the emission from the cathode is negligible compared with the action of the positive ions in ionizing molecules of the gas . . . .; for it is very improbable that the emission from all these metals is the same."

If Dubois' conclusions are correct, and if the action is produced by the change of the photoelectric function γ, there appears to be no reason why γ should not be approximately the same for ordinary metals for the Schumann radiation, which is the radiation chiefly responsible for the photoelectric emission: for, according to Compton and Richardson (Phil. Mag. xxvi. p. 549, 1913), the photoelectric sensitiveness is supposed to be the same for all metals, but for the electronegative metals the curve is shifted bodily towards the region of short wave-lengths. It is obvious then that according to this idea the photoelectric emissivity of metals, whilst differing enormously for visible light (near the threshold frequency), may have no great percentage difference in the region of shorter wave-lengths, that is, in the Schumann radiation region.

Again, it is quite conceivable that ordinary metal electrodes

formed in the same way, may acquire surface films in the discharge, of similar nature and yield similar results.

In conclusion it may be mentioned that Huxley gives no consideration at all, nor any alternative explanation of the experimental results obtained on pure electrodes and gases, and on the surface electrode phenomena described in my papers. He simply neglects the experimental findings altogether.

May 19th, 1927.

XLVII. *The Structure of Xenotime and the Relation between Chemical Constitution and Crystal Structure. By* L. Vegard, *Dr. Philos., Professor of Physics at the University, Oslo* *.

[Plate XV.]

Introduction.

§ 1. In two papers † published in 1916 and 1917 I gave results of investigations on the structure of xenotime (YPO_4), by means of the Bragg ionization method. As is well known, the crystal form of this mineral is very analogous to that of the zircon group (zircon, rutile, kassiterite, etc.), but owing to the fact that xenotime usually is more or less transformed into another crystal structure, it was very difficult to obtain reflexions of the various orders for the different faces. Thus in a first series of measurements I found for the face (111) only a fourth-order reflexion, while zircon also gave reflexions from the orders (1, 2, and 3) for the corresponding face. These experimental data consequently led to an arrangement of the oxygen atoms somewhat different from that of zircon.

Repeating the observations by an improved experimental arrangement and on better crystal material, I found that the (111) face also in the case of xenotime gave reflexions of the orders 1, 2, and 3, and then it appeared that xenotime and zircon gave essentially the same spectra for the faces (100) (110) (001) (101) (111).

All experimental data could then be accounted for by giving xenotime the same crystal structure as zircon.

It was at the same time pointed out that this result had far-reaching consequences with regard to the important

* Communicated by the Author.

† L. Vegard, "Results of Crystal Analysis, III. and IV.," Phil. Mag. xxxii. p. 505 (1916), and xxxiii. p. 395 (1917).

question as to the mutual relationship between chemical constitution and crystal structure.

The result means that compounds of different chemical properties and composed of atoms of different valencies may take up essentially identical atomic arrangements in the solid state and thus be isomorphous as regards crystal structure and crystal form.

A necessary condition for two compounds to take up the same crystal structure is that the two compounds have the same number of corresponding structural units or that they have chemical formulæ of the form A'_{n_1}, A''_{n_2} . . . . $A^{i}_{n_i}$, and α'_{n_1}, α''_{n_2} . . . . , $\alpha^{i}_{n_i}$, where A or α either may be atoms or groups of atoms (radicals).

In a later paper * it was stated that one of the essential conditions to be fulfilled for isomorphous structures was, that the corresponding structural units fulfil certain conditions with regard to the space they require in the lattice †.

It is, however, also certain that the nature of the chemical binding will play a considerable part in determining the atomic arrangement of the atoms. This is evident from the mere fact that elementary substances appear in a great variety of atomic arrangements (space lattices). That the space filling of the atoms is only one factor among several others is also evident from the fact that the crystal structure may be different for chemically analogous substances, although the lattice in question does not involve any volume conditions to be fulfilled. Thus the alkali and ammonium halogenides appear in two different crystal forms, the rock-salt type and the CsCl type.

On account of the importance attached to the structure of the zircon type of crystals, I determined to carry out an analysis of the same group of crystals by means of the powder method. This redetermination of the structure was first carried out for the minerals zircon, rutile, and kassiterite, and the results were described in a paper already published ‡. It appeared that the structure originally

* L. Vegard, *Vid. Selsk. Skr.* i. No. 16, pp. 12 16 (1922); *Zeitschr. f. Phys.* B. 12, pp. 299–303 (1922).

† Recently the same view as to the connexion between chemical constitution and crystal structure has been taken up by Goldschmidt and his collaborator, who in a series of important papers have applied it to a variety of chemical systems. (Geochem. Verteilungsgesetze, IV–VIII, *Vid. Akad. Skr. Mat.-nat. Kl.* Nos. 5 and 7 (1925), No. 1, No. 2, and No. 8 (1926.)

‡ L. Vegard, "Results of Crystal Analysis," *Norsk. Vid. Akad. Skr.* i. No. 11 (1925); Phil. Mag. i. p. 1151 (1926).

found for rutile and kassiterite was confirmed by the new investigations. The structure of zircon, however, had to be somewhat modified as regards the position of the oxygen atoms.

The structure originally found for zircon could be referred to the space group C_{4v}^{11}. Now the zircon lattice might be derived from this space group, but we had to specialize the parameters in such a way that new symmetry elements appeared and the space group of the highest symmetry, to which the zircon lattice was to be referred, was that of D_{4h}^{19}.

Also the structure of rutile and kassiterite may be regarded as derived from the space group C_{4v}^{11} by a certain specification, which, however, raises the symmetry to that of the space group D_{4h}^{14}.

Although zircon was considered to be morphologically isomorphous with rutile and kassiterite, they were not exactly "isomorphous" with regard to internal structure.

If the crystal structure could show the chemical constitution, the structure found would mean that rutile and kassiterite had to be written as $(TiO_2)_2$ and $(SnO_2)_2$, while the formula of zircon would be $Zr(SiO_4)$.

Description of the Experiments.

§ 2. In the present paper I am going to give the results of an analysis of the structure of xenotime undertaken by means of the powder method. It appeared to be difficult to find a crystal material which was so little transformed that the xenotime spectrum became dominating on the film. After having tried several pieces, Dr. O. Hassel was so kind as to give me a specimen which gave very good powder diagrams.

As the dimensions of the elementary lattice (a and c) were found in the earlier investigations by means of the ionization method, the lines on the powder diagram belonging to xenotime were easily identified.

In one case there might be some doubt whether a weak line might be referred to xenotime in the tetragonal form or to the transformed state or impurities. The question was settled by means of the previous spectra obtained with the Bragg spectrometer, and to be quite sure I also took a complete diagram with a rotating crystal. I also had the opportunity of comparing my diagram with rotating crystal with one taken by Dr. Hassel. In these complete diagrams as well as in the spectra obtained by the Bragg method, the transformed substance and impurities do not interfere with the reflexion maxima obtained from the crystal faces of untransformed xenotime.

The powder spectrogram of xenotime on which the present analysis is based is shown on the Plate.

The result of the identification of lines is given in Table I. The relative intensities of the lines as they were

TABLE I.—Xenotime (YPO_4).

a=9·735 Å. c=6·013 Å. c/a=0·6177. α=58°. γ=22°·5.

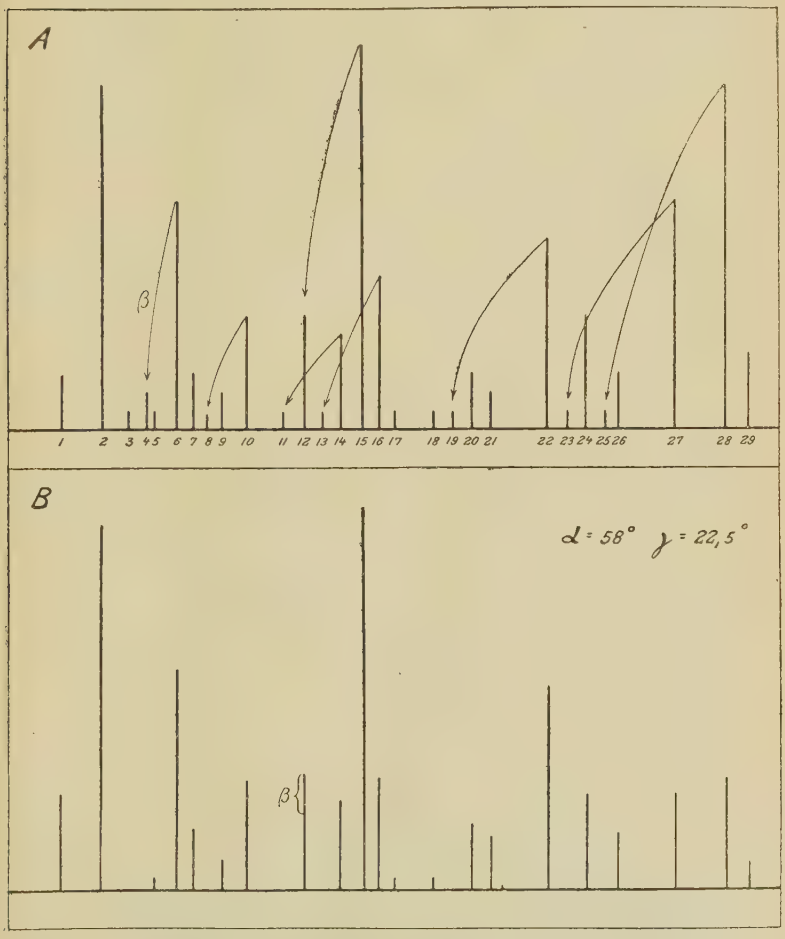
No.	ϕ°.	$\left(\frac{2a}{\lambda}\sin\phi\right)^2$.	$h_1^2+h_2^2+\left(\frac{a}{c}\right)^2 h_3^2$.	Int. Obs.	Int. Cal.	h_1 h_2 h_3.
1	14·520	4·56	4·62	15	25	1 1 1
2	19·393	8·01	8·00	90	95	2 2 0
3	(22·297)	(10·45)	(10·48)	(5)	0	(0 0 2)*
4	24·069	(14·57)	(14·48) β			(2 0 2) β
5	24·758	12·73	12·62	5	3	3 1 1
6	26·579	14·53	14·48	60	57	2 0 2
7	28·006	16·01	16·00	15	16	4 0 0
8	29·040	(20·64)	(20·62) β			(3 3 1) β
9	30·270	18·45	18·48	10	8	2 2 2
10	32·239	20·66	20·62	30	28	3 3 1
11	34·946	(28·75)	(28·62) β			(5 1 1) β
12	36·324	(30·74)	(30·48) β	30	20+β	(4 2 2) β
		25·49	25·59			1 1 3
13	37·112	(31·90)	(32·00) β			(4 4 0) β
14	38·933	28·67	28·62	25	23	5 1 1
15	40·360	30·45	30·48	100	100	4 2 2
16	41·640	32·05	32·00	40	29	4 4 0
17	42·772	33·52	33·59	5	3	3 1 3
18	45·233	36·60	36·62	5	3	5 3 1
19	46·710	(46·42)	(46·48) β			(6 0 2) β
20	47·940	40·02	40·00	15	17	6 2 0
			41·59		7	3 3 3
21	49·072	41·44		10	14	
			41·94		7	0 0 4
			42·48		1	4 4 2
22	53·059	46·38	46·48	50	53	6 0 2
			49·59		0	5 1 3
23	54·487	(58·05)	(57·94) β			(4 0 4) β
24	55·963	49·86	49·94	30	25	2 2 4
			50·48		0	6 2 2
25	57·686	(62·58)	(62·48) β			(6 4 2) β
			52·62		1	5 5 1
26	58·424	52·69		15	15	
			52·62		14	7 1 1
			57·94		21	4 0 4
27	63·149	57·79		60	25	
			57·59		4	5 3 3
			60·62		0	7 3 1
			61·94		7	4 2 4
28	67·924	62·35		90	29	
			62·48		22	6 4 2
29	70·089	64·18	64·00	20	7	8 0 0

* Impurities.

estimated from the spectrogram are given in diagram A of fig. 1.

We now first of all tried whether we could explain the intensities of the lines by means of the structure originally found for zircon and xenotime, but for certain lines there

Fig. 1.



was a disagreement between observed and calculated intensities, which showed—as in the case of zircon—that the atomic arrangement originally found for xenotime had to be somewhat modified. We then naturally tried an atomic arrangement corresponding to the one finally found for zircon.

The coordinates of the basis group of the zircon lattice are given in a previous paper *.

We shall express the coordinates of the basis group of xenotime in the same way as used for zircon, and for the sake of convenience we write down its coordinates. Our unit cell contains 8 molecules. Now all atoms are arranged in face centred lattices, and we merely need to give their coordinates.

$$\left.\begin{array}{ll} \mathrm{Y}: \left[\left[\tfrac{1}{8}, \tfrac{1}{8}, \tfrac{1}{8}\right]\right], & \left[\left[-\tfrac{1}{8}, -\tfrac{1}{8}, -\tfrac{1}{8}\right]\right]; \\ \mathrm{P}: \left[\left[\tfrac{1}{8}, \tfrac{1}{8}, \tfrac{5}{8}\right]\right], & \left[\left[-\tfrac{1}{8}, -\tfrac{1}{8}, \tfrac{3}{8}\right]\right]; \\ \mathrm{O}\begin{cases} \left[\left[\tfrac{1}{8}+\epsilon, \tfrac{1}{8}+\epsilon, \tfrac{1}{8}+\eta\right]\right], & \left[\left[\tfrac{1}{8}-\epsilon, \tfrac{1}{8}-\epsilon, \tfrac{1}{8}+\eta\right]\right], \\ \left[\left[\tfrac{1}{8}-\epsilon, \tfrac{1}{8}+\epsilon, \tfrac{1}{8}-\eta\right]\right], & \left[\left[\tfrac{1}{8}+\epsilon, \tfrac{1}{8}-\epsilon, \tfrac{1}{8}-\eta\right]\right], \\ \left[\left[-\tfrac{1}{8}-\epsilon, -\tfrac{1}{8}-\epsilon, -\tfrac{1}{8}-\eta\right]\right], & \left[\left[-\tfrac{1}{8}+\epsilon, -\tfrac{1}{8}+\epsilon, -\tfrac{1}{8}-\eta\right]\right], \\ \left[\left[-\tfrac{1}{8}+\epsilon, -\tfrac{1}{8}-\epsilon, -\tfrac{1}{8}+\eta\right]\right], & \left[\left[-\tfrac{1}{8}-\epsilon, -\tfrac{1}{8}+\epsilon, -\tfrac{1}{8}+\eta\right]\right]. \end{cases} \end{array}\right\} (1$$

We put

$$\left.\begin{array}{l} 2\pi\epsilon = \alpha, \\ 2\pi\eta = \gamma, \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the structure factor takes the form:

$$\left.\begin{array}{r} \mathrm{S} = \cos \mathrm{A}(\mathrm{Y}+(-1)^{h_3}\mathrm{P}+40\cos h_1\alpha\cos h_2\alpha\cos h_3\gamma) \\ +40\sin \mathrm{A}\sin h_1\alpha\sin h_2\alpha\sin h_3\gamma. \end{array}\right\} \quad (3)$$

$$\mathrm{A} = 2\pi(h_1+h_2+h_3).$$

We distinguish between the three cases:

$$\Sigma h = 4n, \qquad \cos \mathrm{A} = \pm 1, \qquad \sin \mathrm{A} = 0;$$

$$\Sigma h = 4n \pm 1, \qquad \cos \mathrm{A} = \pm \frac{1}{\sqrt{2}}, \qquad \sin \mathrm{A} = \pm \frac{1}{\sqrt{2}};$$

$$\Sigma h = 4n+2, \qquad \cos \mathrm{A} = 0, \qquad \sin \mathrm{A} = \pm 1.$$

It should also be remembered that S is to be multiplied with the structure factor characteristic of the face-centred lattice, but this is either 4 or 0; but when we remember that this factor cuts out all reflexions of planes with mixed indices, we need not take this factor into account.

In the case of zircon we deduced directly from the intensities the parameter values:

$$\alpha = 56^\circ, \qquad \gamma = 20^\circ.$$

* L. Vegard, *Vid. Selsk. Skr.* i. No. 11 (1925); Phil. Mag. i. p. 1151 (1926).

From the condition that one Zr-atom shall have "contact" with eight oxygen atoms, and that the oxygen atoms shall be mutually in "contact," we found the values:

$$\alpha = 58°, \qquad \gamma = 19°{\cdot}3,$$

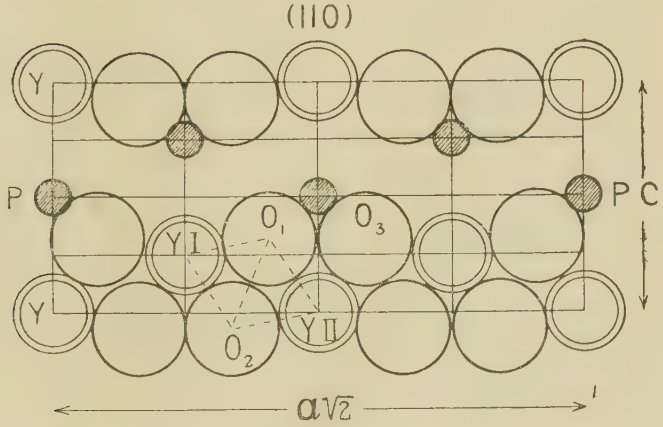
and within the limit of possible error these values coincide with those directly found from the intensity distribution. Thus there is very good reason to believe that the parameters are in accordance with these contact conditions.

In the case of xenotime the corresponding conditions for the centre distances are:

$$\left.\begin{aligned} Y_{(I)} - O &= Y_{(II)} - O_1; \\ O_1 - O_2 &= O_1 - O_3. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (4)$$

The meaning will be seen from fig. 2.

Fig. 2.



From these two equations we obtain the parameter values:

$$\epsilon = 0{\cdot}161, \qquad \alpha = 58°,$$
$$\eta = 0{\cdot}062, \qquad \gamma = 22°{\cdot}5.$$

In addition we tried the following sets of parameter values:

(1) $\alpha = 60°, \qquad \gamma = 30°.$

(2) $\alpha = 56°, \qquad \gamma = 30°.$

(3) $\alpha = 52°, \qquad \gamma = 22°{\cdot}5.$

(4) $\alpha = 56°, \qquad \gamma = 20°.$

All of these four sets of values give fairly good agreement with observed intensities, but in all cases there are some small discrepancies ; thus, in case (1) line No. 14 comes out stronger than 16 contrary to observations. Further, No. 18 comes out too weak.

In case (2) No. 18 is too weak, and No. 27 is too strong as compared with 28.

In case (3) Nos. 5, 7, 17 are too weak, and No. 27 too strong as compared with 28.

In the case (4) Nos. 5, 17 are too weak. In fact we find the best agreement with the parameters $\alpha = 58$ and $\gamma = 22°{\cdot}5$, which fulfil the above-mentioned "contact" conditions.

The relative intensities calculated by means of these parameters are given in fig. 1 B.

It should be noticed that a faint line No. 3 was observed, which happens to coincide with the position of (002) for xenotime, but the intensity of this line should be identically zero. This faint line No. 3, however, is no doubt due to impurities or to the transformed product of xenotime, for neither the ionization method nor the diagrams taken with rotating crystals show any reflexion corresponding to (002); in these diagrams from faces with definite orientation a line due to impurities or transformed substance would not appear.

From the values found for the parameters we can calculate the "diameters" of each of the constituent atoms. For the centre distances we get :

$$O-O = 2{\cdot}45\,\text{Å}, \quad Y-O = 2{\cdot}24\,\text{Å}, \quad P-O = 1{\cdot}66\,\text{Å}.$$

In Table II. we give the quantities determining the xenotime lattice, and for the sake of comparison we have added those of zircon.

TABLE II.

	Xenotime.	Zircon.
a	9·735 Å	9·41 A
c	6·013 „	6·01 „
c/a	0·6177	0·639
ϵ	0·161	0·161
η	0·062	0·0535
ρ_O	1·22 Å	1·18 A
ρ_Y	1·02 „	ρ_{Zr} 0·99 „
ρ_P	0·44 „	ρ_{Si} 0·49 „

Crystal Structure and Atomic Properties.

§ 3. As the result of these investigations we find that xenotime has actually the same structure as zircon, and very nearly the same dimensions and parameters, and the general conclusions which were drawn from this fact in my paper * published in 1917 have been confirmed.

In the case of zircon we have oxygen attached to two four-valent atoms (Zr Si), in the second case we have one three-valent atom (Y) and one five-valent (P), and these differences involve considerable differences as regards chemical forces and constitution.

In order to explain that the two substances show practically the same atomic arrangement, we have to take two facts into account :—

First of all we notice the most suggestive fact that *the sum of the valencies in both cases is equal to* 8. The sum of the valency electrons is equal to the number (8) which should be characteristic of the "surface" system of the inert gases. This fact suggests that although the valencies are unequal for the atoms of the two minerals, they may *in combination form similar electronic systems responsible for the mutual binding of the atoms.*

Secondly, the substances fulfil the condition that *corresponding atoms* (*ions*) *require nearly the same space in the lattice*, or they have about equal "atomic diameters."

The latter condition is in the present case most essential, for the *lattice puts very strong volume conditions on the dimensions of those atoms which are able to form crystals of the same structure and axis ratio* (c/a) *as zircon and xenotime.*

The contact conditions previously mentioned † lead to the following equations:

$$\left.\begin{aligned} \epsilon - \frac{1}{2}\left(\frac{c}{a}\right)^2\eta &= \frac{1}{16}\left\{2+\left(\frac{c}{a}\right)^2\right\}, \\ \epsilon + \frac{1}{2}\left(\frac{c}{a}\right)^2(\eta+4\eta^2) &= \frac{1}{16}\left\{3-\frac{1}{2}\left(\frac{c}{a}\right)^2\right\}. \end{aligned}\right\} \quad . \quad (5)$$

By means of these two equations the parameters ϵ and η are determined as functions of the axis ratio c/a.

Let us now suppose the substance to have the chemical formula ABC_4, then, as we saw, we can find the diameters of A, B, and C as functions of a and (c/a). The equations are easily written, but for the sake of brevity we need only

* L. Vegard, Phil. Mag. xxxiii. p. 421 (1917).

† L. Vegard, *Vid. Selsk. Skr.* i. No. 11 (1925); Phil. Mag. i. p. 1151 (1926).

remark that by introducing the values of the parameters (from 5), we obtain the diameters δ as known functions of a and c/a ; in fact we have

$$\delta = a\phi(c/a),$$

or

$$\frac{\delta_A}{\phi_A\left(\frac{c}{a}\right)} = \frac{\delta_B}{\phi_B\left(\frac{c}{a}\right)} = \frac{\delta_C}{\phi_C\left(\frac{c}{a}\right)}. \quad . \quad . \quad . \quad (6\,a)$$

If the axis ratio c/a is given, $\phi_A(c/a)$, $\phi_B(c/a)$, $\phi_C(c/a)$ are known, and only those atoms which approximately fulfil the condition (6 *a*) can build up a zircon lattice. If the crystals be regarded as isomorphous, they should possess about equal axis ratio c/a ; consequently for substances isomorphous with zircon c/a should be equal to about 0·65, and the atomic diameters should approximately fulfil the relation

$$\frac{\delta_A}{1} = \frac{\delta_B}{0{\cdot}46} = \frac{\delta_C}{1{\cdot}2}. \quad . \quad . \quad . \quad . \quad . \quad (6\,b)$$

If we write rutile $TiTiO_4$ and kassiterite $SnSnO_4$ they are seen to be of the form ABO_4, where A = B. But we see that in this case the relation (6) is not fulfilled, and these substances cannot be exactly isomorphous with zircon, which is in fact in accordance with the structures found for these substances. Thus the strong relation which is claimed by the zircon structure explains the fact that this structure is not exactly isomorphous with that of rutile, although they both lead to nearly equal axis ratios and equal symmetry class, so that they may be said to be morphologically isomorphous. Any substitution of atoms between zircon and xenotime on the one side and rutile and kassiterite on the other should be excluded, or mixed crystals should not exist.

From what has been said it should be essential for the formation of the xenotime and zircon lattice that the sum of the valencies of A and B are equal to 8 and that the atomic diameters have approximately a definite ratio. As the rare earth elements are trivalent, and as most of them under comparable conditions have atomic diameters approximately equal to that of Y, we should expect that a number of substances of the form APO_4, where A is one of the rare earth elements, would form structures isomorphous with that of xenotime.

Now it is to be remembered that the structure found for xenotime is a somewhat unstable one. Xenotime is gradually

changing crystal structure under maintainance of its external form (metamict).

The xenotime structure involves a very close packing of atoms, and in consequence the minerals of this type have a high density. From the measured dimensions of the lattice we find the density of xenotime to be

$$\rho = 4{\cdot}23.$$

(Abegg, 'Handbuch der anorganischen Chemie,' gives 4·45—4·70. These somewhat higher values are no doubt to be explained by impurities. The values found from the X-ray analysis correspond to the pure substance.)

The dense packing and the unstability of the lattice indicate that the atoms of xenotime do not fulfil the volume conditions of the lattice so well as those of zircon, so the atoms in a similar way as in mixed crystals have to suffer a certain accommodation of their natural atomic (or ionic) diameters. This exercises a certain internal strain, which causes the gradual transformation. This instability will be counterbalanced if we put the substance under high pressure, because we know from thermodynamics that increase of pressure will have a tendency to produce such a state, which requires a small volume.

This would suggest that a mineral like xenotime is formed under high pressure.

Now in his 'Chemische Kristallographie' Groth states that YPO_4 usually contains impurities of the phosphates of the rare earth elements, which indicates that xenotime forms mixed crystals with phosphates of the rare earth elements, or Y atoms are irregularly substituted by atoms of the rare earth elements La, Ce, Pr, ... etc.

When the rare earth elements become dominating, their phosphates are no longer stable in the zircon lattice, but they take up a monocline structure (monazite). It might, however, be possible that the phosphates of the rare earth elements assume zircon structure under high pressures and in certain intervals of temperature.

The results of my early investigations * on mixed crystals of alkali and ammonium haloides present a striking analogy to this case. At ordinary temperature the substances KCl and NH_4Cl *e. g.* have a different crystal structure; but still in the lattice of KCl more than 20 per cent. of the K atoms

* L. Vegard, "Konstitution der Mischkristalle und die Raumfüllung der Atome," *Vid. Selsk. Skr.* i. No. 6 (1921) (Com. Nov. 30, 1920) *Zeitschr. f. Phys.* B. v. p. 17 (1921).

can be substituted with (NH_4) groups, and from the expansion of the lattice I could by means of the additivity law calculate the dimensions of the NH_4Cl lattice of the face centred KCl type. In this case we know that also pure NA_4Cl at temperatures above 159° C. takes up the face-centred KCl structure.

If we limit our considerations to elements A and B, for which the sum of the positive valencies is equal to 8, we are led to regard a large number of combinations of elements with regard to their ability of forming crystals of the zircon type.

As long as we let oxygen be the third element, the volume conditions require that the radius of the positive A ion is equal to about 1 Å and that of the B ion equal to about 0·4–0·5 Å. In the case when both A and B are four-valent (zircon type), we have to consider the possibility that either Zr or Si may be replaced by another four-valent positive ion. Then the following elements come into consideration : C, Ti (rare earth elements), Th, Ge, Sn, Pb.

A substitution of Si with any of these elements would violate the volume conditions (6).

A substitution of Zr should be excluded for the elements Ge, Sn, Ti, which have too small ionic dimensions.

The diameters of the four-valent positive ions of rare earth elements and the ions Pb (+4) and Th (+4) according to Goldschmidt * are nearly equal to that of Zr (+4).

We have therefore to reckon with the possibility that crystals with zircon structure may be formed by substances where Zr in zircon is substituted with Th, Pb, or some of the rare earth elements.

As a matter of fact the Th compound is known as the mineral Thorite ($ThSiO_4$), which is isomorphous with zircon †, but in the case of thorite the zircon arrangement is unstable and the zircon type of thorite is gradually transformed (metamict form). As in the case of xenotime, this is explained from the fact that the diameter differs from that claimed by volume conditions, and the lattice is only stable at very high pressure.

As to the existence of the lead compound, I find no references in the literature.

When A is three-valent and B five-valent as in the case of xenotime (YPO_4), the atoms B, Al, Se, and the rare earth

* V. M. Goldschmidt, *Det Norske Vid. Akad. Skr.* i. No. 2 (1926).

† See P. Groth, *Chem. Krist.* i. p. 85, and L. Vegard, Phil. Mag. xxxii. p. 93 (1916).

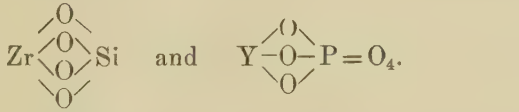
elements may come into consideration, but out of these, as already mentioned, only the rare earth elements approximately fulfil the volume conditions. According to Goldschmidt, Tl as trivalent positive ion has a diameter about equal to that of Y, and therefore from the point of view of volume conditions a compound $TlPO_4$ might exist in the zircon type of lattice.

If A is two-valent and B is six-valent, a substitution of B with Se (+6) and A by Ca (+2) would approximately fulfil the volume conditions. Further, A might be substituted by Be and B by Cr. Thus the substances $CaSeO_4$ and $BeCrO_4$ approximately fulfil the volume conditions required by the zircon structure.

New possibilities would arise when we imagine O substituted by another element, and by means of the volume conditions (6) we should for each substituent of O be able to find out which compounds might possibly possess a structure of the zircon type.

As stated in a previous paper *, similar volume conditions were applied to explain the fact that the anatase structure of TiO_2 only exists in the case of titanium and not for the other elements of the same group. It is of interest to notice that also the structure found for the scheelite group of minerals * leads to fairly strong volume conditions, and by similar considerations we may perhaps understand why a number of analogous substances do not exist with the same crystal structure as that of scheelite.

If we look at the crystal structure of zircon and xenotime from the point of view of their chemical constitution formula, we find that the old way of expressing the chemical constitution would lead to the formulæ:



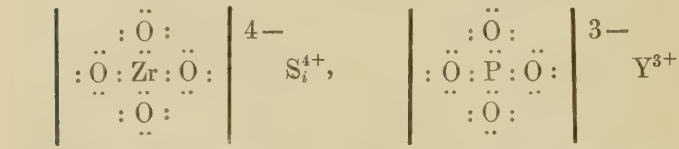
According to these formulæ there should be an essential difference with regard to the chemical constitution of the two substances. In zircon all four oxygen atoms should be equal, while in xenotime one of them should take up a singular position. In the crystal, however, all four oxygen atoms are equal. Either we should have to conclude that the chemical constitution does not come to expression in the

* L. Vegard, *Vid. Selsk. Skr.* i. No. 11 (1925); Phil. Mag. i. p. 1151 (1926).

atomic arrangement in the crystal, or we have to find new expressions for the chemical constitution.

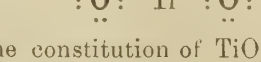
Now the way of expressing the chemical constitution, which in later years has been introduced by Werner, Lewis, Langmuir, and Kossel, leads to the following formulæ:

Zircon. Xenotime.



According to these formulæ we have for both minerals a saturated complex of the form MO_4, with 8 "surface" electrons round each atom, where all oxygen atoms are equal. In the case of zircon the complex carries 4, in the case of xenotime 3 negative elementary charges. These formulæ are thus in perfect agreement with the atomic arrangement in the crystals.

In this connexion it is of interest to notice that the atomic arrangement of rutile (and isomorphous substances) as well as the atomic structure of anatase correspond to a chemical formula $(TiO_2)_x$. The way in which we write the constitution formula very much depends on the value of x. Putting $x=1$, the constitution formula might be written:



In any case the constitution of TiO_2 and SnO_2 should be essentially different from that of zircon and xenotime, and this difference has found its expression in the crystal structure, in spite of the fact that rutile and zircon on account of analogy as regards form and symmetry properties have been considered as isomorphous. This isomorphism, however, does not apply to internal structure, but merely to external form and morphological symmetry.

Summary of Results.

1. The structure of xenotime has been investigated by means of the powder method and the results verified by comparison with rotating crystal diagrams.

2. The result previously obtained—that xenotime and zircon have practically identical space lattices—has been confirmed.

3. The important consequences, which were drawn in a paper of 1917 from the identity of zircon and xenotime

structure relating to the connexion between chemical constitution and crystal structure, have thus been found valid.

4. In the xenotime lattice all four oxygen atoms are equal, while the old chemical constitution formula would put one of the four oxygen atoms in a singular position. The assumption of the formation of a complex MO_4 with a constitution in accordance with the theories of Werner, Lewis, Langmuir, or Kossel, however, leads to a perfect agreement between the atomic arrangement in the solid state and the constitution formula.

5. In accordance with views expressed in papers published in 1921, one of the factors which may determine the crystal structure is that each atom requires certain space. A great many structures, however, give no volume conditions whatever, and in these cases the nature of the atomic forces is the dominating factor which determines the atomic arrangement. In the case of xenotime, however, the parameter values directly derived from the intensities of the reflexion maxima of the powder diagrams lead to a very close packing of the atoms, and the contact conditions lead to a definite condition with regard to the diameters of those atoms which can form lattices of the zircon type. In this case only substances for which the atoms approximately fulfil the volume conditions of the lattice will be able to form crystals of the zircon type. A number of such possibilities have been mentioned.

6. When the volume conditions are only approximately fulfilled, the lattice is likely to be unstable, but on account of the close packing a lattice of the zircon type may still be stable under very high pressure. Metamict substances like xenotime and thorite have probably been formed under very high pressure. Under ordinary pressure the lattice becomes unstable, and a new more stable lattice is formed under gradual transformation of the minerals.

My sincere thanks are due to Dr. O. Hassel for putting at my disposal a good specimen of xenotime and also photograms of xenotime taken with a rotating crystal. I also wish to express my sincere thanks to Mr. S. Stensholt for his excellent assistance in connexion with these investigations.

Physical Institute,
University, Oslo.
May 11, 1927.

XLVIII. *Heat Regeneration and Regenerative Cycles. By* Wm. J. Walker, *D.Sc., Ph.D., Professor of Mechanical Engineering, University of the Witwatersrand, Johannesburg* *.

Summary.

The following paper sets out to investigate the possibilities in heat regenerative cycles, particularly in relation to internal combustion turbine development. A new type of regenerative cycle is proposed, the analysis of which indicates the independence of turbine thermal efficiency on compression ratio. Actually it appears that the thermal efficiency should be higher the lower the compression ratio. The efficiency required of the regenerator unit, however, becomes lower the higher the compression ratio, so that the problem becomes the experimental one of determining the lowest compression ratio at which a regenerator can be designed to meet the conditions imposed.

So far as thermodynamic cycles are concerned, methods of heat regeneration may be divided into the two classes :—

1. External heat regeneration.
2. Internal heat regeneration.

In the first method the exhaust heat from one prime mover is diverted to another source of supply, such as a steam boiler, and utilized indirectly in another prime mover actuated by the steam produced. The distinctive feature of the method is that the discharged heat is not returned again to take part in a cycle of events similar in all respects to that through which it has just passed.

The second or internal method of heat regeneration has many points of interest, but, possibly owing to somewhat unfortunate ventures in the past in connexion with the development of hot-air engines, it does not appear that any serious attempt has ever been made to investigate its implications in the case of what are now known to be workable thermodynamic cycles for internal combustion engines. The distinctive feature of this method is that some of the rejected heat of a cycle is transferred back again to the fresh charge of working fluid, for the carrying out of the next cycle. The author's investigations into the general nature of this problem have led to certain interesting results which may prove to have some value as a guide to future developments, particularly in gas-turbine evolution.

* Communicated by the Author.

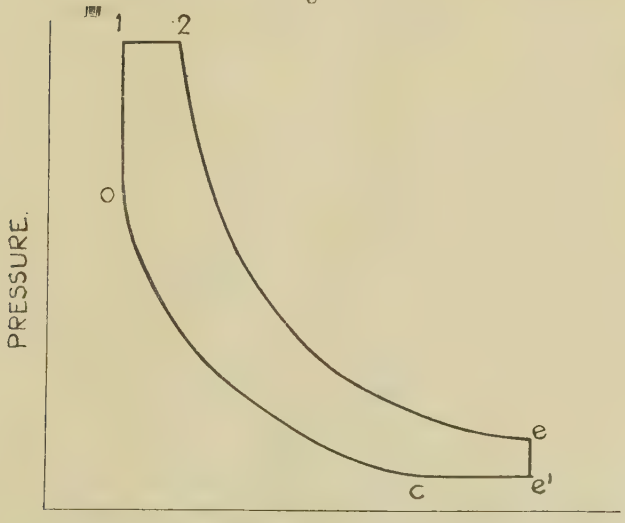
In the classic method of analysing regenerative cycles, each cycle is considered as comprising four general operations as follows in the given order :—

(*a*) Isothermal compression at T_2, say.
(*b*) Heat reception.
(*c*) Isothermal expansion at $T_1 > T_2$.
(*d*) Heat rejection.

If the regenerator efficiency is assumed to be unity, the whole of the heat rejected at (*d*) is returned during the heat-reception period (*b*), with the net result that (*b*) and (*d*) combined involve neither loss nor gain of heat, and therefore become equivalent to two adiabatic processes. All perfect regenerative cycles of this type have, therefore, the same efficiency as a Carnot cycle between the same temperature limits. Such are the Stirling and Ericcson air cycles with constant volume and constant pressure regeneration respectively. In practice both these cycles failed to realize anything like expectations, because

(1) They involve external combustion of the fuel ;
(2) Perfect regeneration cannot be realized ;
(3) Isothermal compression and expansion are practical impossibilities.

Fig. 1.



Turning now, however, to the possibilities of internal heat regeneration when applied to internal combustion cycles, consider the basic dual combustion cycle of fig. 1. Assuming

that the exhaust gases discharged at temperature T_e are to be used to heat up the supply gases, the most that can be done, theoretically, is to raise the temperature of the latter, by some type of regenerator, also to temperature T_e. In this case, it should be noted, the regenerator does not require to be of unit efficiency, since the exhaust heat discharged is equal to $K_V(T_e-T_{e'})+K_P(T_{e'}-T_c)$, while, assuming that $T_e<T_1$, that given to the supply gases is $K_V(T_e-T_0)$, which is evidently less. The efficiency of the cycle is given by

$$\eta_t=\frac{\text{Work done}}{\text{Heat received from external sources}}$$

$$=\frac{\text{Heat received from external+internal sources}-\text{Heat rejected}}{\text{Heat received from external sources}}$$

$$=1-\frac{\text{Heat rejected}-\text{Heat received from internal sources}}{\text{Heat received from external sources}}$$

$$=1-\frac{K_V(T_e-T_{e'})+K_P(T_{e'}-T_c)-K_V(T_e-T_0)}{K_V(T_1-T_e)+K_P(T_2-T_1)}$$

$$=1-\frac{K_P(T_{e'}-T_c)-K_V(T_{e'}-T_0)}{K_V(T_1-T_e)+K_P(T_2-T_1)},$$

which, substituting all temperatures in terms of T_c, becomes

$$\eta_t=1-\frac{m(\beta-1)-(\beta-r^{m-1})}{\alpha\{r^{m-1}-\rho^m/\beta^{m-1}+mr^{m-1}(\rho-1)\}}, \quad . \quad (1)$$

where

$$r=\text{compression ratio}=\frac{V_e}{V_0},$$

$$\alpha=\text{explosion ratio}=\frac{P_1}{P_0},$$

$$\rho=\text{cut-off ratio}=\frac{V_2}{V_1},$$

$$\beta=\text{extended expansion ratio}=\frac{V_e}{V_c}.$$

For the constant volume cycle, assuming regeneration along these lines to be incorporated, $\rho=1$ and $\beta=1$, so that the efficiency from (1) becomes

$$\eta_t=1-\frac{1}{\alpha}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

yielding the somewhat unexpected result that the efficiencies of regenerative cycles of this type are independent of the compression ratio r and the adiabatic index m; an interesting conclusion in view of the importance of these factors in non-regenerative cycles.

The foregoing has been deduced under the assumption of

constant specific heats of gases. The actual efficiency under variable specific heat conditions is given, to a first and close approximation *, by

$$\eta_t' = \left(1-\frac{1}{\alpha}\right)\left\{1-\frac{\lambda T_c}{2}(\alpha+1)\right\}$$
$$= 1-\frac{1}{\alpha}-\frac{\lambda T_c}{2}\left(\frac{\alpha^2-1}{\alpha}\right), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and evidently increases with α, *i. e.* with the amount of fuel burned per cycle.

It is evident, however, that there are serious practical difficulties in the way of such constant volume regeneration. Constant pressure regeneration is a much more realizable process here, and since it is generally agreed that the constant pressure cycle is the one most applicable to gas-turbine operation, it is natural to investigate such a possibility on the same lines as the foregoing analysis.

It should first be noted that the constant pressure regenerative cycle efficiency cannot be deduced from (1), owing to the discontinuity at point 1 on the cycle, and the consequent uncertainty as to whether or not the regenerated heat will extend its effect past that point. It is obvious from the foregoing that it has been assumed not to have passed that point, *i. e.* T_e is implicitly assumed less than T_1. If, however, $T_1 < T_e$ and the regenerated heat is added between T_1 and T_2, the efficiency becomes

$$\eta_t = 1-\frac{K_V(T_e-T_{e'})+K_P(T_{e'}-T_c)-K_P(T_e-T_1)}{K_P(T_2-T_e)}$$

which, by reducing as before, gives

$$\eta_t = 1-\frac{(\alpha\rho^m/\beta^{m-1}-\beta)+m(\beta-1)-m(\alpha\rho^m/\beta^{m-1}-\alpha r^{m-1})}{m(\alpha\rho r^{m-1}-\alpha\rho^m/\beta^{m-1})}.$$

For the constant pressure cycle $\alpha=1$ and $\beta=\rho$, and if this regenerative principle is included, the efficiency becomes

$$\eta_t = 1-\frac{1}{\rho}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

analogous to expression (3).

The corresponding variable specific heat efficiency becomes

$$\eta_t' = 1-\frac{1}{\rho}-\frac{\lambda T_c}{2}\left(\frac{\rho^2-1}{\rho}\right). \quad . \quad . \quad . \quad . \quad (5)$$

Although, however, these regenerative cycle efficiencies are independent of compression ratio, such is not the case with the regenerator efficiencies demanded by the systems of regeneration proposed. In the case of the constant volume

* Phil. Mag. Sept. 1917.

cycle, this would evidently be

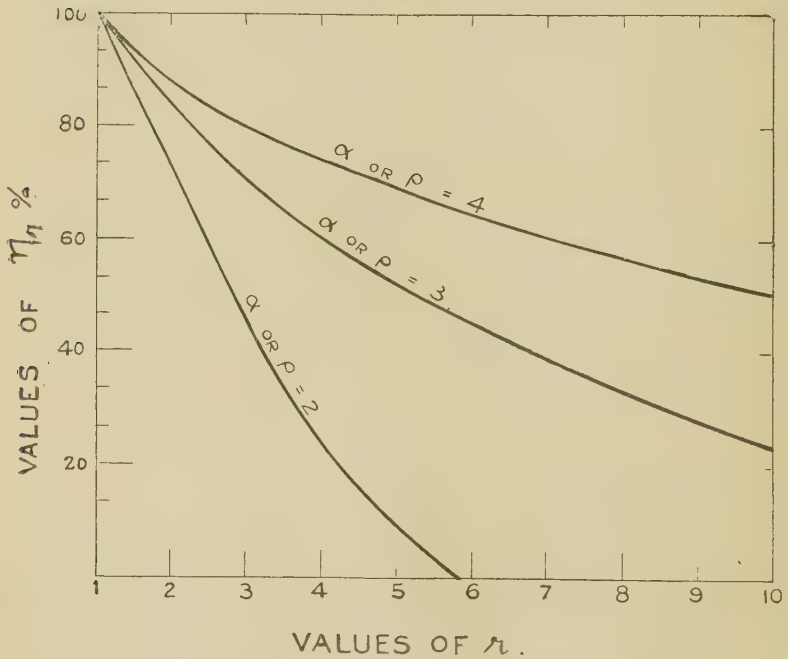
$$\eta_r = \frac{K_V(T_e - T_0)}{K_V(T_e - T_c)} = \frac{\alpha - r^{m-1}}{\alpha - 1} \quad . \quad . \quad . \quad . \quad (6)$$

For the constant pressure cycle

$$\eta_r = \frac{K_P(T_e - T_1)}{K_P(T_{e'} - T_c)} = \frac{\rho - r^{m-1}}{\rho - 1} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Fig. 2 shows the variation of η_r with the compression ratio r for different values of α and ρ in (6) and (7). Clearly, the higher the compression ratio the lower does

Fig. 2.



the regenerator efficiency require to be to meet the conditions imposed by this method of regeneration.

Should the principle of regeneration here outlined ever become the object of experimental inquiry in connexion with gas-turbine development, the obvious line of approach will be to determine the lowest compression ratio at which the regenerator can meet the conditions imposed. This follows from the fact that, besides conducing to a high mechanical efficiency and to a low value of negative work, a low compression ratio for a given air/fuel ratio will result in a high value of ρ the cut-off ratio, and so yield a high thermal efficiency.

XLIX. *A Class of Integral Equations occurring in Physics*, *By* D. M. Wrinch, *M.A., D.Sc., and* J. W. Nicholson. *M.A., D.Sc., F.R.S.**

THE integral equations and identities to be discussed in this communication are becoming fundamental in certain classes of physical problems. Their "interest" has recently been mainly in relation to problems of seismology. One of the equations is widely known and is usually referred to as the Bateman-Herglotz equation, though its history can be traced much further. It is usually quoted† in the form :—

If

$$\phi(p) = p\int_p^a \frac{f'(\eta)\,d\eta}{(\eta^2-p^2)^{1/2}},$$

then

$$f(\eta) = -\frac{2}{\pi}\int_\eta^a \frac{\phi(\lambda)\,d\lambda}{(\lambda^2-\eta^2)^{1/2}} + C, \quad . \quad . \quad . \quad (1)$$

where C is some constant. It is used in this form in the application to problems of seismology which are of considerable importance—as emphasized, for example, by Prof. Lamb in his Presidential Address to the British Association in 1925.

The problems of seismology do not, however, exhaust the more immediate uses of this result and others with which it is associated. It is at least of equal importance in problems concerned with the diffraction of waves round certain types of obstacle. But quite apart from these applications, the discussion of this integral equation and the associated equations and identities is of importance in view of the relation between them and the fundamental Bessel-Fourier theorems and equations.

The Bateman-Herglotz equation goes back essentially to Abel‡, whose general result is usually quoted§ in the form :—

If $0<\sigma<1$ and

$$\chi(\eta) = \int_\nu^\eta \frac{\phi(\zeta)\,d\zeta}{(\eta-\zeta)^\sigma}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

then

$$\phi(\xi) = \frac{\sin\sigma\pi}{\pi}\frac{\partial}{\partial\xi}\int_\nu^\xi \frac{\chi(\eta)\,d\eta}{(\xi-\eta)^{1-\sigma}}. \quad . \quad . \quad (3)$$

* Communicated by the Authors.

† *Vide e. g.* Jeffreys, 'The Earth,' p. 219 (Camb. Univ. Press, 1924).

‡ Collected Works, p. 11 ; Crelle's Journal, vol. i. p. 153 (1826).

§ Bôcher, 'Integral Equations,' p. 8 (Camb. Univ. Press).

Abel generalized this equation from the particular case of $\sigma=\frac{1}{2}$, which he encountered in connexion with the problem of the tautochrone, and though his solution of it was correct the proof was in some ways unsatisfactory. The form given above is appropriate for the case when $\eta>\nu$. There is of course a related equation when $\eta<\nu$ which with its solution may be exhibited as follows :—

If $0<\sigma<1$ and

$$\chi(\eta)=\int_{\eta}^{\nu}\frac{\phi(\zeta)\,d\zeta}{(\zeta-\eta)^{\sigma}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

then

$$\phi(\xi)=-\frac{\sin\sigma\pi}{\pi}\frac{\partial}{\partial\xi}\int_{\xi}^{\nu}\frac{\chi(\eta)\,d\eta}{(\eta-\xi)^{1-\sigma}}, \quad . \quad (5)$$

and it is of this equation that the Bateman-Herglotz equation is a particular case. For, writing $\sigma=\frac{1}{2}$ and

$$\xi=x^2,\ \eta=y^2,\ \zeta=z^2,\ \nu=\gamma^2,\ \chi(\eta)=g(y)/y,\ \phi(\xi)=f(x)/2x,$$

it may be written in the form :—

If

$$g(y)/y=\int_{y}^{\gamma}\frac{f(z)\,dz}{(z^2-y^2)^{1/2}}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

then

$$f(x)=-\frac{2}{\pi}\frac{\partial}{\partial x}\int_{x}^{\gamma}\frac{g(y)\,dy}{(y^2-x^2)^{1/2}}. \quad . \quad . \quad (7)$$

Thus the Bateman-Herglotz equation is a special case of Abel's equation.

In Abel's form as originally quoted it was necessary that $\chi(\nu)=0$, in order that the equation might have a solution. This restriction was removed by Goursat *, who at the same time provided for the existence of solutions of a discontinuous character. In view of applications to physics and more especially to problems of wave diffraction, Goursat's advance in the study of the equation is of fundamental importance. The restriction nevertheless persists in some of the methods of establishing the equation †.

The first proof published, which can be regarded as free from the main difficulties of Abel's method, was due to Liouville ‡, who appears to have been unaware of Abel's work.

* *Acta Math.* xxvii. p. 131 (1903),

† *Cp. e.g.* Bateman, Phil. Mag. xix. p. 576 *et seq.* (1910).

‡ *Journal de l'Ecole Polytechnique*, xxi. p. 1 (1832); Liouville's Journal, iv. p. 233 (1839).

That this equation in the special case $\sigma = \frac{1}{2}$ was the fundamental equation regulating the propagation of earthquake waves was first perceived by Herglotz *, who discussed it in a new manner. Subsequently Bateman † independently gave a discussion and in fact rediscovered the theorem.

In the present communication we are concerned with the development of the complete class of integral equations—of which the Bateman-Herglotz equation is a member—and their solutions, and with the interesting identities which present themselves in a systematic survey. It is also shown in the present paper that there is an intimate relation between them and the Bessel-Fourier results.

The Bessel-Fourier results to which we refer comprise the following. Firstly, Fourier's theorem

$$f(x) = \frac{2}{\pi}\int_0^\infty \cos\lambda x\, d\lambda \int_0^\infty \cos\lambda\mu f(\mu)\, d\mu \quad . \quad (8)$$

or its equivalent,—if

$$G(\lambda) = \int_0^\infty \cos\lambda\mu f(\mu)\, d\mu, \quad . \quad . \quad . \quad (9)$$

then

$$f(x) = \frac{2}{\pi}\int_0^\infty \cos\lambda x\, G(\lambda)\, d\lambda, \quad . \quad . \quad . \quad (10)$$

exhibiting the function f as the solution of the integral equation (3) for a known form of G, which is known to be unique. Secondly, there is the Bessel-Fourier theorem

$$f(x) = \int_0^\infty \lambda J_0(\lambda x)\, d\lambda \int_0^\infty \mu J_0(\lambda\mu) f(\mu)\, d\mu$$

or its equivalent,—if

$$G(\lambda) = \int_0^\infty \mu J_0(\lambda\mu) f(\mu)\, d\mu,$$

then

$$f(x) = \int_0^\infty \lambda J_0(\lambda x)\, G(\lambda)\, d\lambda.$$

Both these theorems are applicable to a function which is continuous except at a finite number of discontinuities provided that it has limited total fluctuation in the range 0 to ∞.

The Fourier theorem is, of course, a special case of the Bessel-Fourier theorem when stated in the general form

$$f(\rho) = \int_0^\infty \lambda J_n(\lambda\rho)\, d\lambda \int_0^\infty \mu J_n(\lambda\mu) f(\mu)\, d\mu \quad (n > -1), \quad (11)$$

which was established for integral values of n by Hankel

* *Phys. Zeit.* viii. p. 145 (1907). † *Loc. cit.*

and subsequently extended to non-integral values by Sonine * and others. For when $n=-\frac{1}{2}$ it yields

$$f(\rho)=\frac{2}{\pi}\int_0^\infty \frac{\lambda}{(\lambda\rho)^{1/2}}\cos\lambda\rho\, d\lambda\int_0^\infty \frac{\mu}{(\lambda\mu)^{1/2}}\cos\lambda\mu\, f(\mu)\, d\mu$$

or

$$\rho^{1/2}f(\rho)=\frac{2}{\pi}\int_0^\infty \cos\lambda\rho\, d\lambda\int_0^\infty \cos\lambda\mu\,.\,\mu^{1/2}f(\mu)\, d\mu,$$

which is the Fourier theorem for the function $\rho^{1/2}f(\rho)$. By taking $n=\frac{1}{2}$ we obtain, in the same manner, the sine form of Fourier's theorem.

In deriving the theorems of this paper from these Bessel-Fourier results, the conditions satisfied by the arbitrary functions employed are specified at the outset. And with this point of departure we are, moreover, free from the necessity of proving any "existence" theorems in connexion with the subsequent results.

In addition to the Bessel-Fourier theorem and Fourier's theorem, there exist four useful results which may be regarded as "hybrids" of these two. It was in fact in connexion with these mixed theorems that it became apparent that there was an interesting relation between the equations and identities under discussion and the fundamental Bessel-Fourier theorem. We therefore begin by briefly indicating these hybrids.

Four Mixed Theorems.

If the function $\phi(x)$ satisfy Fourier's cosine formula, then

$$\phi(y)=\frac{2}{\pi}\int_0^\infty \cos\lambda y\, d\lambda\int_0^\infty \cos\lambda\mu\,\phi(\mu)\, d\mu.$$

Thus

$$\phi(by)=\frac{2}{\pi}\int_0^\infty \cos\lambda by\, d\lambda\int_0^\infty \cos\lambda\mu\,\phi(\mu)\, d\mu$$

and

$$\frac{1}{b}\frac{\partial}{\partial y}\phi(by)=-\frac{2}{\pi}\int_0^\infty \lambda\sin\lambda by\, d\lambda\int_0^\infty \cos\lambda\mu\,\phi(\mu)\, d\mu. \quad (12)$$

Now † if $\frac{1}{2}>m>-1$,

$$\mathrm{J}_{-m-\frac{1}{2}}(k)=\frac{k^{m+\frac{1}{2}}/\pi^{1/2}}{2^{m-\frac{1}{2}}\Gamma(1+m)}\int_0^\infty \sin(k\cosh q)\,(\sinh q)^{2m+1}\, dq. \quad (13)$$

* Sonine, *Math. Ann.* xvi. (1880).

† Sonine, *l. c.*

Thus, multiplying (12) by $(b^2-1)^{\frac{2m+1}{2}}$ and writing

$$b = \cosh q$$

and integrating with respect to q from 0 to ∞, we get, taking the right-hand side first,

$$\int_0^\infty \left(\frac{\lambda y}{2}\right)^{-\frac{1}{2}-m} J_{-m-\frac{1}{2}}(\lambda y)\lambda\, d\lambda \int_0^\infty \cos\lambda\mu\, \phi(\mu)\, d\mu$$

$$= -\frac{\pi^{1/2}}{4\Gamma(1+m)}\frac{\partial}{\partial y}\int_0^\infty \frac{\phi(y\cosh q)(\sinh q)^{2m+1}\, dq}{\cosh q}, \quad (14)$$

a theorem whose particular case $m=-\frac{1}{2}$, namely

$$\int_0^\infty \lambda J_0(\lambda y)\, d\lambda \int_0^\infty \cos\lambda\mu\, \phi(\mu)\, d\mu$$

$$= -\frac{\partial}{\partial y}\int_0^\infty \phi(y\cosh q)\, dq/\cosh q, \quad (15)$$

is of great interest and usefulness.

Again, using Fourier's sine formula we have

$$\frac{1}{a}\frac{\partial}{\partial y}\phi(ay) = \frac{2}{\pi}\int_0^\infty \lambda\cos\lambda ay\, d\lambda \int_0^\infty \sin\lambda\mu\, \phi(\mu)\, d\mu, \quad (16)$$

and in view of the formula due also to Sonine *,

$$J_{m+\frac{1}{2}}(k)$$

$$= \frac{k^{m+\frac{1}{2}}/\pi^{1/2}}{2^{m+\frac{1}{2}}\Gamma(1+m)}\int_0^{\pi/2} \cos(k\sin\phi)(\cos\phi)^{2m+1}\, d\phi, \ (m>-1),$$

. . . (17)

if we write

$$a = \sin\theta.$$

Multiply (16) on both sides by $(1-a^2)^{\frac{2m+1}{2}}$ and integrate with respect to θ from 0 to $\pi/2$, and we get

$$\int_0^{\pi/2} \left(\frac{\lambda y}{2}\right)^{-m-\frac{1}{2}} J_{m+\frac{1}{2}}(\lambda y)\,.\,\lambda d\lambda \int_0^\infty \sin\lambda\mu\, \phi(\mu)\, d\mu$$

$$= +\frac{\pi^{1/2}}{\Gamma(1+m)}\frac{\partial}{\partial y}\int_0^{\pi/2} \frac{\phi(y\sin\theta)(\cos\theta)^{2m+1}}{\sin\theta} d\theta, \quad (18)$$

the second mixed theorem, which in the particular case $m=-\frac{1}{2}$ is of special interest and takes the form

$$\int_0^{\pi/2} \lambda J_0(\lambda y)\, d\lambda \int_0^\infty \sin\lambda\mu\, \phi(\mu)\, d\mu$$

$$= \frac{\partial}{\partial y}\int_0^{\pi/2} \phi(y\sin\theta)\, d\theta/\sin\theta. \quad (19)$$

* *Loc. cit.*

Again, starting from the cosine form of Fourier's theorem with $\mu f(\mu)$ for the function, we obtain

$$\frac{by}{a} f(by) = \frac{2}{\pi}\int_0^\infty \cos(bayt)\, dt \int_0^\infty \mu \cos(at)\, \mu f(\mu)\, d\mu.$$

Take $a = \frac{1}{b}$ and for any positive value of a

$$\frac{y}{a^2} f\left(\frac{y}{a}\right) = \frac{2}{\pi}\int_0^\infty \cos yt\, dt \int_0^\infty \mu \cos(at) \mu f(\mu)\, d\mu. \quad (20)$$

If now we multiply both sides of (20) by $(1-a^2)^{m+\frac{1}{2}}$ and write

$$a = \sin\theta$$

and integrate from $\theta = 0$ to $\theta = \frac{\pi}{2}$, we get

$$\int_0^\infty \cos yt\, dt \int_0^\infty \left(\frac{t\mu}{2}\right)^{-m-\frac{1}{2}} \mathrm{J}_{m+\frac{1}{2}}(t\mu) \,.\, \mu f(\mu)\, d\mu$$

$$= \frac{\pi^{1/2}}{\Gamma(1+m)} y \int_0^{\pi/2} \frac{(\cos\theta)^{2m+1} f(y/\sin\theta)}{\sin^2\theta}\, d\theta, \quad (21)$$

which is the third of the mixed theorems and like the other mixed theorems yields an interesting particular case when $m = -\frac{1}{2}$, namely

$$\int_0^\infty \cos yt\, dt \int_0^\infty \mu \mathrm{J}_0(\mu t) f(\mu)\, d\mu = y \int_0^{\pi/2} \frac{f(y/\sin\theta)}{\sin^2\theta}\, d\theta, \quad (22)$$

or, by the transformation

$$\sin\theta = \operatorname{sech} q,$$

$$\int_0^\infty \cos yt\, dt \int_0^\infty \mu \mathrm{J}_0(\mu t)\, f(\mu)\, d\mu = y \int_0^\infty \cosh q\, f(y \cosh q)\, dq.$$

. . . (23)

After the same manner, starting with the sine formula applied to the function $\mu f(\mu)$, we get

$$\frac{ay}{b} f(ay) = \frac{2}{\pi}\int_0^\infty \sin(bayt)\, dt \int_0^\infty \mu \sin(bt) \mu f(\mu)\, d\mu,$$

and taking again $ab = 1$,

$$\frac{y}{b^2} f\left(\frac{y}{b}\right) = \frac{2}{\pi}\int_0^\infty \sin yt\, dt \int_0^\infty \mu \sin(bt) \mu f(\mu)\, d\mu,$$

whence, by means of (17), we get the result

$$\int_0^\infty \sin yt\, dt \int_0^\infty \left(\frac{\mu t}{2}\right)^{-\frac{1}{2}-m} \mathrm{J}_{m+\frac{1}{2}}(\mu t) \cdot \mu f(\mu)\, d\mu$$

$$\doteq \frac{\pi^{1/2}}{\Gamma(1+m)} \cdot y \int_0^\infty \frac{(\sinh q)^{2m+1} f(y/\cosh q)}{\cosh^2 q}\, dq, \quad (24)$$

the fourth mixed theorem whose particular case when $m = -\frac{1}{2}$ is

$$\int_0^\infty \sin yt\, dt \int_0^\infty \mu \mathrm{J}_0(\mu t) f(\mu)\, d\mu = y \int_0^\infty f(y/\cosh q)\, dq/\cosh^2 q, \quad (25)$$

or, with $\cosh q = \operatorname{cosec} \theta$,

$$\int_0^\infty \sin yt\, dt \int_0^\infty \mu \mathrm{J}_0(\mu t) f(\mu)\, d\mu = y \int_0^{\pi/2} f(y \sin\theta) \sin\theta\, d\theta.$$

These four hybrid theorems and more especially their particular cases when $m + \frac{1}{2} = 0$ are of great value in applications to integrals involving the Bessel functions, though derived so simply. Many of the proofs given by Sonine and others of such integrals can be considerably shortened if these results are used. Macdonald * has given similar indications from the Bessel-Fourier theorem itself.

Thus taking as a specific example

$$\phi(\mu) = \mu e^{-p\mu}$$

and applying theorem (15), we get

$$-\frac{\partial}{\partial y} \cdot y \int_0^\infty e^{-py\cosh q}\, dq = \int_0^\infty \lambda \mathrm{J}_0(\lambda y)\, dy \int_0^\infty \mu \cos\lambda\mu\, e^{-p\mu}\, d\mu$$

or

$$\frac{\partial}{\partial y} \cdot [y \mathrm{K}_0(py)] = \int_0^\infty \lambda \mathrm{J}_0(\lambda y) \left(\frac{\partial}{\partial p} \cdot \frac{p}{p^2+\lambda^2}\right) d\lambda,$$

whence

$$\frac{\partial}{\partial p} \cdot p \mathrm{K}_0(py) = \frac{\partial}{\partial p} \cdot p \int_0^\infty \frac{\lambda \mathrm{J}_0(\lambda y)\, d\lambda}{p^2+\lambda^2},$$

which is true by Basset's theorem †

$$\mathrm{K}_0(py) = \int_0^\infty \frac{\lambda \mathrm{J}_0(\lambda y)\, d\lambda}{p^2+\lambda^2}.$$

* Proc. Lond. Math. Soc. vol. xxxv. (1902).

† Due, however, originally to Mehler, *Journal für Math.* lxviii., as pointed out by Watson.

The further development of such identities is not, however, at present relevant to our purpose.

We now pass on to the derivation of a class of integral equations, including Abel's theorem in its generality, from the Bessel-Fourier and Fourier theorems.

The Fundamental Theorems.

As before, if $\phi(y)$ satisfy Fourier's sine formula,

$$\phi(y) = \frac{2}{\pi}\int_0^\infty \sin \lambda y \, d\lambda \int_0^\infty \sin \lambda\mu \, \phi(\mu) \, d\mu,$$

then

$$\begin{aligned}\phi(ay) &= \frac{2}{\pi}\int_0^\infty \sin \lambda a y \, d\lambda \int_0^\infty \sin \lambda\mu \, \phi(\mu) \, d\mu \\ &= \frac{2b}{\pi}\int_0^\infty \sin \lambda a b y \, dt \int_0^\infty \sin b\mu t \, \phi(\mu) \, d\mu,\end{aligned}$$

where b is any positive quantity. If $by = x$, then if we write

$$\phi(\mu) = \mu f(\mu),$$

it follows that

$$\frac{ax}{b^2} \cdot f\left(\frac{ax}{b}\right) = \frac{2}{\pi}\int_0^\infty \sin axt \, dt \int_0^\infty \sin b\mu t \, f(\mu) \, \mu d\mu \quad (26)$$

and

$$\frac{\partial}{\partial x} \cdot \frac{x}{b^2}\left(\frac{1-a^2}{b^2-1}\right)^{\frac{1}{2}-\sigma} f\left(\frac{ax}{b}\right)$$

$$= \frac{2}{\pi}\int_0^\infty (1-a^2)^{\frac{1}{2}-\sigma} \sin a\,xt\,t dt \int_0^\infty (b^2-1)^{\sigma-\frac{1}{2}} \sin b\mu t \, f(\mu) \, \mu d\mu. \quad (27)$$

We now use the formula (13) for $n = \sigma - 1$ and the formula (17) for $m = -\sigma$.

Thus writing

$$a = \sin\theta, \qquad b = \cosh q,$$

and integrating our equation on both sides, with respect to θ from 0 to $\pi/2$ and with respect to q from 0 to ∞, we

find

$$\frac{\partial}{\partial x}\cdot x\int_0^\infty \frac{(\sinh q)^{2\lambda-1}}{\cosh^2 q}\,dq\int_0^{\pi/2}\frac{f(x\sin\theta/\cosh q)}{(\cos\theta)^{2\lambda-1}}\,d\theta$$

$$=\tfrac{1}{2}\Gamma(1-\sigma)\,\Gamma(\sigma)\int_0^\infty \mathrm{J}_{\frac{1}{2}-\sigma}(xt)\;(xt)^{\sigma-\frac{1}{2}}\,t\,dt$$

$$\times\int_0^\infty \mathrm{J}_{\frac{1}{2}-\sigma}(\mu t)\;(\mu t)^{\frac{1}{2}-\sigma}\,\mu f(\mu)\,d\mu$$

$$=\frac{\pi}{2\sin\sigma\pi}x^{\sigma-\frac{1}{2}}\int_0^\infty t\,\mathrm{J}_{\frac{1}{2}-\sigma}(xt)\,dt$$

$$\times\int_0^\infty \mu\,\mathrm{J}_{\frac{1}{2}-\sigma}(\mu t)\,\mu^{\frac{1}{2}-\sigma}f(\mu)\,d\mu$$

$$=\frac{\pi}{2\sin\sigma\pi}f(x)$$

by the Bessel Integral Theorem for the function $\mu^{\frac{1}{2}-\sigma}f(\mu)$. Thus we have the fundamental formula

$$\text{(A)}\quad f(x)=\frac{2}{\pi}\sin\sigma\pi\,\frac{\partial}{\partial x}\cdot x\int_0^\infty\frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\,dq$$

$$\times\int_0^\infty\frac{f(x\sin\theta/\cosh q)}{(\cos\theta)^{2\sigma-1}}\,d\theta. \quad (28)$$

With the substitutions

$$\cosh q=x/y,\qquad \sin\theta=z/y,$$

it becomes

$$f(x)=\frac{2}{\pi}\sin\sigma\pi\,\frac{\partial}{\partial x}\cdot x\int_0^x\frac{dy/x}{(x^2/y^2-1)^{1-\sigma}}\int_0^y\frac{f(z)\,dz/y}{(1-z^2/y^2)^\sigma}$$

$$=\frac{2}{\pi}\sin\sigma\pi\,\frac{\partial}{\partial x}\cdot\int_0^x\frac{y\,dy}{(x^2-y^2)^{1-\sigma}}\int_0^y\frac{f(z)\,dz}{(y^2-z^2)^\sigma}. \quad (29)$$

An alternative pair of substitutions,

$$\sin\theta=\lambda/x,\qquad \cosh q=\lambda/\mu,$$

leads to

$$f(x)=\frac{2}{\pi}\sin\sigma\pi\,\frac{\partial}{\partial x}\cdot x\int_0^x\frac{d\lambda/x}{(1-\lambda^2/x^2)^\sigma}\int_0^\lambda\frac{f(\mu)\,d\mu/\lambda}{(\lambda^2/\mu^2-1)^{1-\sigma}}$$

$$=\frac{2}{\pi}\sin\sigma\pi\,\frac{\partial}{\partial x}\cdot x^{2\sigma}\int_0^x\frac{d\lambda/\lambda}{(x^2-\lambda^2)^\sigma}\int_0^\lambda\frac{\mu^{2-2\sigma}f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}}. \quad (30)$$

After the same manner, if we take Fourier's cosine formula

$$\phi(y) = \frac{2}{\pi}\int_0^\infty \cos\lambda y\, d\lambda \int_0^\infty \cos\lambda\mu\, \phi(\mu)\, d\mu,$$

we may deduce the consequence,

$$\frac{\partial}{\partial x}\cdot\frac{x}{a^2}\left(\frac{1-a^2}{b^2-1}\right)^{\frac{1}{2}-\sigma} f\left(\frac{bx}{a}\right) = -\frac{2}{\pi}\int_0^\infty (b^2-1)^{\sigma-\frac{1}{2}} \sin b\,xt\; t\, dt \times \int_0^\infty (1-a^2)^{\frac{1}{2}-\sigma} \cos a\mu t f(\mu)\,.\,\mu\, d\mu,$$

and obtain the corresponding equation,

$$\text{(B)}\quad f(x) = -\frac{2}{\pi}\sin\sigma\pi\frac{\partial}{\partial x}\cdot x\int^{\pi/2}\frac{(\cos\theta)^{-2\sigma+1}}{\sin^2\theta}\,d\theta \times \int_0^\infty \frac{f(x\cosh q/\sin\theta)}{(\sinh q)^{1-2\sigma}}\,dq, \quad (31)$$

the companion to (28). And with the substitutions

$$\sin\theta = x/y, \qquad \cosh q = z/y,$$

it becomes

$$f(x) = -\frac{2}{\pi}\sin\sigma\pi\frac{\partial}{\partial x}\int_x^\infty \frac{y\,dy}{(y^2-x^2)^\sigma}\int_y^\infty \frac{f(z)\,dz}{(z^2-y^2)^{1-\sigma}}. \quad (32)$$

An alternative pair of substitutions,

$$\cosh q = \lambda/x, \qquad \sin\theta = \lambda/\mu,$$

leads to

$$f(x) = -\frac{2}{\pi}\sin\sigma\pi\frac{\partial}{\partial x}\cdot x^{2-2\sigma}\int_x^\infty \frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_\lambda^\infty \frac{\mu^{2\sigma} f(\mu)\,d\mu}{(\mu^2-\lambda^2)^\sigma}\,. \quad . \quad . \quad . \quad (33)$$

The Application of Theorem A to a function which is zero for parts of its range.

Suppose now that we apply the theorem (A),

$$f(x) = \frac{2}{\pi}\sin\sigma\pi\frac{\partial}{\partial x}\cdot x\int_0^\infty \frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\,dq \times \int_0^{\pi/2}\frac{f(x\sin\theta/\cosh q)\,d\theta}{(\cosh\theta)^{2\sigma-1}},$$

to a function $f(x)$ which is zero for x between 0 and γ, and zero also for x between δ and ∞. Then if we perform the

integrations only over the area belonging to a region, in any geometrical representation, defined by

$$0 \leq q \leq \infty, \quad 0 \leq \theta \leq \pi/2,$$

and to cases where

$$\gamma \leq z \sin\theta/\cosh q \leq \delta,$$

we shall be able to deduce that

$$\frac{2}{\pi} \sin \sigma\pi \cdot x \int_0^\infty \frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\, dq \int_0^{\pi/2} \frac{f(x \sin\theta/\cosh q)\, d\theta}{(\cosh\theta)^{2\sigma-1}}$$
$$= C_1 \quad x < \gamma$$
$$= C_2 \quad x > \delta,$$

where C_1 and C_2 are independent of x, and the integrations are of functions equivalent to zero over portions of their range. Moreover, we also have

$$\frac{2}{\pi} \sin \sigma\pi \cdot \frac{\partial}{\partial x} x \int_0^\infty \frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\, dq \int_0^{\pi/2} \frac{f(x \sin\theta/\cosh q)\, d\theta}{(\cos\theta)^{2\sigma-1}}$$
$$= f(x) \quad \lambda < x < \delta,$$

where in each case the integrations are performed over the restricted area.

If we write

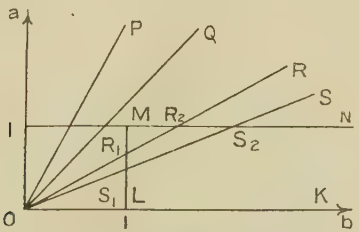
$$\cosh q = b, \qquad \sin\theta = a,$$

and treat a and b as Cartesian coordinates, we have to integrate over the area common to the rectangle

$$a = 0, \quad a = 1, \quad b = 1, \quad b = \infty,$$

and the sector

$$\frac{\gamma}{x} < \frac{a}{b} < \frac{\delta}{x}.$$



There are evidently three cases to discuss. And it will be convenient for purposes of exposition to refer to the diagram in which the various lines OP, OQ, OR, OS represent various lines of the form a/b = constant.

Case 1 *C.* $x < \gamma < \delta$.

In this case the lines

$$\frac{a}{b} = \frac{\gamma}{x}, \quad \frac{a}{b} = \frac{\delta}{x}$$

are represented by OQ and OP respectively, and the sector QOP bounded by these lines and the rectangle KLMN bounded by the lines

$$a = 0, \quad b = 1, \quad a = 1, \quad b = \infty,$$

have no point in common. There is therefore no area over which to integrate, and we therefore merely arrive at the fact that $f(x)$ is zero.

Case 2 *C.* $\gamma < x < \delta$.

In this case the sector is QOR and it and the rectangle KLMN have in common the triangle R_1MR_2 over which the integration has therefore to be carried out. Thus we have

$$\frac{\pi}{2\sin\sigma\pi} f(x) = \frac{\partial}{\partial x} \cdot x \int_0^{\cosh^{-1} x/\gamma} \frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\, dq \times \int_{\sin^{-1}(\nu\cosh q/x)}^{\pi/2} \frac{f(x\sin\theta/\cosh q)}{(\cos\theta)^{2\sigma-1}}\, d\theta,$$

$$\sin\theta = z/y.$$

Writing $\cosh q = x/y$, we get

$$\frac{\pi}{2\sin\sigma\pi} f(x) = \frac{\partial}{\partial x} \cdot \int_\gamma^x \frac{y\, dy}{(x^2-y^2)^{1-\sigma}} \int_\gamma^y \frac{f(x)\, dz}{(y^2-z^2)^\sigma}, \quad (34)$$

or with

$$x^2 = \xi, \quad y^2 = \eta, \quad z^2 = \zeta, \quad \gamma^2 = \nu, \quad f(x)/x = \phi(\xi),$$

$$\frac{\pi}{\sin\sigma\pi}\phi(\xi) = \frac{\partial}{\partial\xi}\int_\nu^\xi \frac{d\eta}{(\xi-\eta)^{1-\sigma}} \int_\nu^\eta \frac{\phi(\zeta)\, d\zeta}{(\eta-\zeta)^\sigma} \quad (\nu \leq \xi).$$

And this result is Abel's theorem for $\xi \geq \nu$.

For these two equivalent results may also obviously be expressed in the form of integral equations and their solutions. Thus, if

$$g(y) = \int_\gamma^y \frac{f(z)\, dz}{(y^2-z^2)^\sigma},$$

then

$$f(x) = \frac{2\sin\sigma\pi}{\pi} \frac{\partial}{\partial x} \int_\gamma^x \frac{y g(y)\, dy}{(x^2-y^2)^{1-\sigma}}. \quad . \quad . \quad (35)$$

Similarly, if

$$\chi(\eta) = \int_\nu^\eta \frac{\phi(\zeta)\, d\zeta}{(\eta - \zeta)^\sigma},$$

then

$$\phi(\xi) = \frac{\sin \sigma\pi}{\pi} \frac{\partial}{\partial} \int_\nu^\xi \frac{\chi(\eta)\, d\eta}{(\xi - \eta)^{1-\sigma}}. \quad . \quad . \quad . \quad (36)$$

The above conclusions were reached by integrating over the triangle R_1MR_2 by means of strips parallel to the a-axis. If, however, we integrate over strips parallel to the b-axis, we obtain the theorem—equivalent of course to the theorem previously obtained—

$$\frac{\pi}{2 \sin \sigma\pi} f(x) = \frac{\partial}{\partial x} \cdot x \int_{\sin^{-1}(\gamma/x)}^{\pi/2} \frac{d\theta}{(\cos\theta)^{2\sigma-1}} \times \int_0^{\cosh^{-1}(x \sin\theta/\gamma)} \frac{f(x \sin\theta/\cosh q)}{(\sinh q)^{1-2\sigma} \cosh^2 q}\, dq.$$

Taking new variables λ, μ given by

$$\lambda = x \sin\theta, \qquad \mu = \lambda/\cosh q,$$

we find

$$\frac{\pi}{2 \sin \sigma\pi} f(x) = \frac{\partial}{\partial x} \cdot x^{2\sigma} \int_\gamma^x \frac{d\lambda/\lambda}{(x^2 - \lambda^2)^\sigma} \int_\gamma^\lambda \frac{\mu^{2-2\sigma} f(\mu)\, d\mu}{(\lambda^2 - \mu^2)^{1-\sigma}}, \quad (37)$$

or with

$$x^2 = s, \quad \lambda^2 = t, \quad \mu^2 = u, \quad \lambda^2 = \rho, \quad f(x)/x = \phi(s),$$

$$\frac{\pi}{\sin \sigma\pi} \phi(s) = \frac{\partial}{\partial s} \cdot s^\sigma \int_\rho^s \frac{dt/t}{(s-t)^\sigma} \int_\rho^t \frac{u^{1-\sigma} \phi(u)\, du}{(t-u)^{1-\sigma}}. \quad (38)$$

These results also can be expressed in the form of integral equations and their solutions. Thus, if

$$h(\gamma) = \int_\gamma^\lambda \frac{\mu^{2-2\sigma} f(\mu)\, d\mu}{(\lambda^2 - \mu^2)^{1-\sigma}},$$

then

$$f(x) = \frac{2 \sin \sigma\pi}{\pi} \frac{\partial}{\partial x} \cdot x^{2\sigma} \int_\gamma^x \frac{h(\lambda)\, d\lambda/\lambda}{(x^2 - \lambda^2)^\sigma}, \quad . \quad . \quad (39)$$

where σ can have any value between zero and unity, and γ is any constant less than λ. Similarly, if

$$\theta(t) = \int_\rho^t \frac{u^{1-\sigma} \phi(u)\, du}{(t-u)^{1-\sigma}},$$

then

$$\phi(s) = \frac{\sin \sigma\pi}{\pi} \frac{\partial}{\partial s} \cdot s^{\sigma} \int_{\rho}^{s} \frac{\theta(t)\, dt/t}{(s-t)^{\sigma}}, \quad . \quad . \quad (40)$$

where σ can range between zero and unity, and ρ is any constant less than t.

The results (39, 40) containing arbitrary constants σ (lying between 0 and 1) and γ (which is less than x) are of considerable generality. If we take the degenerate case when $\sigma = \frac{1}{2}$ and $\gamma = 0$, the resulting equation is of interest. For if we put

$$h(\lambda) = \lambda k(\lambda),$$

(39) becomes :

If

$$k(\lambda) = \int_0^{\lambda} \frac{\mu f(\mu)\, d\mu/\lambda}{(\lambda^2 - \mu^2)^{1/2}},$$

then

$$f(x) = \frac{2}{\pi} \frac{\partial}{\partial x} \cdot x \int_0^{x} \frac{k(\lambda)\, d\lambda}{(x^2 - \lambda^2)^{1/2}}.$$

Examples of this theorem are already familiar in physics. Writing

$$\lambda = x \sin \phi, \qquad \mu = \lambda \sin \theta,$$

we deduce that if

$$k(\lambda) = \int_9^{\pi/2} f(\lambda \sin \theta) \sin \theta\, d\theta,$$

then

$$f(x) = \frac{2}{\pi} \frac{\partial}{\partial x} \cdot x \int_0^{\pi/2} k(x \sin \phi)\, d\phi.$$

A simple case to consider as an illustration of this theorem is

$$f(x) = \mathrm{J}_0(x).$$

We then have

$$k(\lambda) \int_0^{\pi/2} \mathrm{J}_0(\lambda \sin \theta) \sin \theta\, d\theta = \sin \lambda/\lambda,$$

by a well-known formula. And

$$f(x) = \frac{2}{\pi} \frac{\partial}{\partial x} \cdot x \int_0^{\pi/2} \sin (x \phi) \frac{d\phi}{x \sin \phi}$$

$$= \frac{2}{\pi} \int_0^{\pi/2} \cos (x \sin \phi)\, d\phi = \mathrm{J}_0(x),$$

and the theorem is verified. As a second illustration let

$$k(\lambda) = \cos a\lambda,$$

where a is constant. Then

$$f(x) = \frac{2}{\pi}\frac{\partial}{\partial x}.\, x\int_0^{\pi/2}\cos(ax\sin\phi)\,d\phi$$

$$= \frac{2}{\pi}\frac{\partial}{\partial x}.\, x\frac{\pi}{2}\mathrm{J}_0(ax),$$

or

$$f(x) = \frac{\partial}{\partial x}x\,\mathrm{J}_0(ax) = \frac{\partial}{\partial a}a\,\mathrm{J}_0(ax).$$

Thus

$$k(\lambda) = \int_0^{\pi/2}\frac{\partial}{\partial a}.\, a\,\mathrm{J}_0(a\lambda\sin\theta)\,.\,\sin\theta\,d\theta$$

$$= \frac{\partial}{\partial a}\cdot\left(a\,.\frac{\sin a\lambda}{a\lambda}\right) = \cos a\lambda,$$

and the theorem is again verified.

It is also of interest to point out that some remarkable formulæ can be obtained by using the logarithmic Bessel functions for f or k; and it will in general be found very difficult to establish them in a more direct manner.

Case 3 C. $\gamma < \delta < x$.

The last case when x is greater than γ and δ gives a result of a rather different nature. For, for these values of x, $f(x)$ is zero and therefore we obtain an integral identity satisfied by an arbitrary function.

For the sector ROS and the rectangle KLMN have in common the quadrilateral $\mathrm{R_1R_2S_2S_1}$ over which the integration has to be carried out. And we therefore have

$$\mathrm{C} = x\int_0^{\cosh^{-1}x/\delta}\frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\,dq \times \int_{\sin^{-1}(\gamma\cosh q/x)}^{\sin^{-1}(\delta\cosh q/x)}\frac{f(x\sin\theta/\cosh q)}{(\cos\theta)^{2\sigma-1}}\,d\theta$$

$$+ x\int_{\mathrm{cosh}^{-1}x/\delta}^{\cosh^{-1}x/\gamma}\frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\,dq \int_{\sin^{-1}(\gamma\cosh q/x)}^{\pi/2}\frac{f(x\sin\theta/\cosh q)}{(\cos\theta)^{2\sigma-1}}\,d\theta,$$

where C is a constant, independent of x.

Using again the same substitutions

$$\cosh q = x/y, \quad \sin\theta = z/y,$$

we get

$$C = \int_\delta^x \frac{y\,dy}{(x^2-y^2)^{1-\sigma}} \int_\gamma^\delta \frac{f(z)\,dz}{(y^2-z^2)^\sigma} + \int_\gamma^\delta \frac{y\,dy}{(x^2-y^2)^{1-\sigma}} \int_\gamma^y \frac{f(z)\,dz}{(y^2-z^2)^\sigma}.$$

This interesting theorem is true for x greater than γ and δ.

To find the value of C we can make $x \to \infty$. Then the second integral vanishes like $1/x^{2-2\sigma}$. The first becomes with $y = x\mu$,

$$\begin{aligned} \operatorname*{lt}_{x\to\infty} \int_\delta^x \frac{y\,dy}{(x^2-y^2)^{1-\sigma}} \int_\gamma^\delta \frac{f(z)\,dz}{(y^2-z^2)^\sigma} &= \operatorname*{lt}_{x\to\infty} \int_{\delta/x}^1 \frac{\mu\,d\mu}{(1-\mu^2)^{1-\sigma}} \int_\gamma^\delta \frac{f(z)\,dz}{(\mu^2-z^2/x^2)^\sigma} \\ &= \int_0^1 \mu^{1-2\sigma}(1-\mu^2)^{\sigma-1}\,d\mu \int_\gamma^\delta f(z)\,dz \\ &= \tfrac{1}{2}\int_0^1 (1-t)^{\sigma-1} t^{-\sigma}\,dt \int_\gamma^\delta f(z)\,dz, \end{aligned}$$

with $\mu^2 = t$. Since

$$\int_0^1 (1-t)^{m-1} t^{n-1}\,dt = \Gamma(m)\,\Gamma(n)/\Gamma(m+n),$$

we may evaluate the t-integral and we obtain

$$\begin{aligned} C &= \tfrac{1}{2}\left[\Gamma(\sigma)\,\Gamma(1-\sigma)/\Gamma(1)\right] \int_\gamma^\delta f(z)\,dz \\ &= \frac{\pi}{2\sin\pi\sigma} \int_\gamma^\delta f(z)\,dz. \end{aligned}$$

Thus we have the result—when $x > \delta > \gamma$,

$$\int_\delta^x \frac{y\,dy}{(x^2-y^2)^{1-\sigma}} \int_\gamma^\delta \frac{f(z)\,dz}{(y^2-z^2)^\sigma} + \int_\gamma^\delta \frac{y\,dy}{(x^2-y^2)^{1-\sigma}} \int_\gamma^y \frac{f(z)\,dz}{(y^2-z^2)^\sigma} = \frac{\pi}{2\sin\pi\sigma} \int_\gamma^\delta f(z)\,dz. \quad (41)$$

It is perhaps desirable to verify this formula in one individual case, though special cases are, in general, more difficult to prove than the general formula.

Taking first $\sigma = \frac{1}{2}$, $\gamma = 0$, we deduce

$$\frac{\pi}{2}\int_0^\delta f(z)\,dz = \int_\delta^x \frac{y\,dy}{(x^2-y^2)^{1/2}}\int_0^\delta \frac{f(z)\,dz}{(y^2-z^2)^{1/2}} + \int_0^\delta \frac{y\,dy}{(x^2-y^2)^{1/2}}\int_0^y \frac{f(z)\,dz}{(y^2-z^2)^{1/2}} \quad (x>\delta), \qquad (42)$$

itself an identity of considerable interest. Then selecting the simplest case $f(z)=1$ for verification, the first integral on the right is

$$\begin{aligned} \mathrm{I}_1 &= \int_\delta^x \frac{y\,dy}{(x^2-y^2)^{1/2}}\int_0^\delta \frac{dz}{(y^2-z^2)^{1/2}} \\ &= \int_\delta^x \frac{\sin^{-1}(\delta/y)\;y\,dy}{(x^2-y^2)^{1/2}} \\ &= \Big[\sin^{-1}\delta/y - (x^2-y^2)^{1/2}\Big]_\delta^x - \delta\int_\delta^x \frac{(x^2-y^2)^{1/2}}{(y^2-\delta^2)^{1/2}}\frac{dy}{y} \\ &= \frac{\pi}{2}(x^2-\delta^2)^{1/2} - \delta\int_\delta^x \Big(\frac{x^2-y^2}{y^2-\delta^2}\Big)^{1/2}\frac{dy}{y}. \end{aligned}$$

With the evaluation of the usual type

$$y^2 = \delta^2\cos^2\phi + x^2\sin^2\phi,$$

we find

$$\mathrm{I}_1 = \frac{\pi}{2}(x^2-\delta^2)^{1/2} - \delta(x^2-\delta^2)\int_0^{\pi/2}\frac{\cos^2\phi\,d\phi}{\delta^2\cos^2\phi + x^2\sin^2\phi}.$$

The evaluation of this integral follows well-known lines and we find ultimately that

$$\mathrm{I}_1 = \frac{\pi}{2}(x^2-\delta^2)^{1/2} - \frac{\pi}{2}(x-\delta).$$

Further, the second integral on the right is

$$\begin{aligned} \mathrm{I}_2 &= \int_0^\delta \frac{y\,dy}{(x^2-y^2)^{1/2}}\int_0^y \frac{dz}{(y^2-z^2)^{1/2}} \\ &= \frac{\pi}{2}\int_0^\delta \frac{y\,dy}{(x^2-y^2)^{1/2}} \\ &= \frac{\pi}{2}\Big[-(x^2-y^2)^{1/2}\Big]_0^\delta \\ &= \frac{\pi}{2}[x-(x^2-\delta^2)^{1/2}]. \end{aligned}$$

Thus

$$I_1 + I_2 = \frac{\pi}{2}\delta = \frac{\pi}{2}\int_\delta^\delta dx,$$

so that the theorem is verified.

We obtained the above identity by carrying out the integration over the strips parallel to one axis which make up the quadrilateral $R_1R_2S_2S_1$. If we take steps parallel to the other axis we obtain a result which, though equivalent to the former, is of independent interest. Thus we have

$$C = x\int_{\sin^{-1}(\gamma/x)}^{\sin^{-1}(\delta/x)} \frac{d\theta}{(\cos\theta)^{2\sigma-1}} \times \int_0^{\cosh^{-1}(x\sin\theta/\gamma)} \frac{f(x\sin\theta/\cosh q)}{\cosh^2 q\,(\sinh q)^{2\sigma-1}}\,dq + x\int_{\sin^{-1}(\delta/x)}^{\pi/2} \frac{d\theta}{(\cos\theta)^{2\sigma-1}} \times \int_{\cosh^{-1}(x\sin\theta/\gamma)}^{\cosh^{-1}(x\sin\theta/\delta)} \frac{f(x\sin\theta/\cosh q)}{\cosh^2 q\,(\sinh q)^{2\sigma-1}}\,dq,$$

where C is a constant independent of x. Using again the same substitutions as before, namely,

$$\lambda = x\sin\theta, \qquad \mu = \lambda/\cosh q,$$

we find

$$C = x^{2\sigma}\int_\gamma^\delta \frac{d\lambda/\lambda}{(x^2-\lambda^2)^\sigma}\int_\gamma^\lambda \frac{\mu^{2-2\sigma}f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}} + x^{2\sigma}\int_\delta^x \frac{d\lambda/\lambda}{(x^2-\lambda^2)^\sigma}\int_\gamma^\delta \frac{\mu^{2-2\sigma}f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}},$$

with C constant as regards x.

To find the value of C we may for the sake of variety make x tend to δ. Then C, which is a function of γ and δ, is given by

$$C(\gamma,\delta) = \operatorname*{lt}_{x\to\delta} x^{2\sigma}\int_\gamma^\delta \frac{d\lambda/\lambda}{(x^2-\lambda^2)^\sigma}\int_\gamma^\lambda \frac{\mu^{2-2\sigma}f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}},$$

the second integral evidently being zero when $x=\delta$, and therefore

$$C(\gamma,\delta) = \delta^{2\sigma}\int_\gamma^\delta \frac{d\lambda/\lambda}{(\delta^2-\lambda^2)^\sigma}\int_\gamma^\lambda \frac{\mu^{2-2\sigma}f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}}.$$

Now using theorem (41) for $x=\delta$, we have

$$\frac{\partial}{\partial\delta}C(\gamma,\delta) = \frac{\pi}{2\sin\sigma\pi}f(\delta).$$

Thus

$$C(\gamma, \delta) = \frac{\pi}{2 \sin \delta\pi} \int_\gamma^\delta f(t)\, dv,$$

the lower limit γ being necessary since C when $\gamma = \delta$ is clearly zero. Thus we have the identity

$$\int_\gamma^\delta \frac{\delta\lambda/\lambda}{(x^2-\lambda^2)^\sigma} \int_\gamma^\lambda \frac{\mu^{2-2\sigma} f(\mu)\, d\mu}{(\lambda^2-\mu^2)^{1-\sigma}} + \int_\delta^x \frac{d\lambda/\lambda}{(x^2-\lambda^2)^\sigma} \int_\gamma^\delta \frac{\mu^{2-2\sigma} f(\mu)\, d\mu}{(\lambda^2-\mu^2)^{1-\sigma}}$$

$$= \frac{\pi}{2 \sin \sigma\pi}\, x^{-2\sigma} \int_\gamma^\delta f(\mu)\, d\mu. \qquad x > \delta > \gamma. \quad . \quad (43)$$

This result containing two arbitrary constants γ and δ which can range up to x and the arbitrary constant σ which may range from zero to unity is of very considerable generality, and contains the necessary analytical machinery appropriate for simple application to problems of mathematical physics whose solution requires specific conditions,—in type, that a function or its derivate takes constant values over certain given boundaries,—to be satisfied. It is applicable to important forms of boundaries not hitherto discussed.

We have discussed the application of the theorem

$$f(x) = \frac{2}{\pi} \sin \sigma\pi\, \frac{\partial}{\partial x} \cdot x \int_0^\infty \frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\, dq \int_0^{\pi/2} \frac{f(x \sin\theta/\cosh q)\, d\theta}{(\cos\theta)^{2\sigma-1}}$$

to a function $f(x)$ which is zero for x between 0 and γ and between δ and ∞. To complete the scheme we now apply the theorem to the case of a function $f(x)$ which is zero between γ and δ and not between 0 and γ, nor between δ and ∞, and companion formulæ may be deduced.

In this case the integrations must be performed over that part of the area

$$0 < q \leq \infty, \quad 0 \leq \theta \leq \pi/2$$

in which

$$\gamma \nless x \sin\theta/\cosh q \nless \delta.$$

In terms of a and b, the area over which the integrations have to be performed is the part of the rectangle KLMN

$$a = 0, \quad b = 1, \quad a = 1, \quad b = \infty.$$

which lies *outside* the sector bounded by the lines

$$\frac{a}{b} = \frac{\gamma}{x}, \quad \frac{a}{b} = \frac{\delta}{x}.$$

We take the various cases in the same order as before and only a brief explanation is necessary to demonstrate the results.

Case 1 *D.* $x<\gamma<\delta$.

In this case the sector is represented by QOP and in consequence the integration is taken over the whole of the rectangle KLMN and we find that

$$\frac{\pi}{2\sin\sigma\pi}f(x)=\frac{\partial}{\partial x}\cdot x\int_0^\infty\frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\,dq\int_0^{\pi/2}\frac{(fx\sin\theta/\cosh q)}{(\cos\theta)^{2\sigma-1}}\,d\theta$$

$$=\frac{\partial}{\partial x}\int_0^x\frac{y\,dy}{(x^2-y^2)^{1-\sigma}}\int_0^y\frac{f(z)\,dz}{(y^2-z^2)^\sigma}$$

$$\frac{\pi}{2\sin\sigma\pi}f(x)=\frac{\partial}{\partial x}\cdot x^{2\sigma}\int_0^x\frac{d\lambda/\lambda}{(x^2-\lambda^2)^\sigma}\int_0^\lambda\frac{\mu^{2-2\sigma}f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}},$$

which are, of course, the original theorems (29) and (30).

The next case is more interesting.

Case 2 *D.* $\gamma<x<\delta$.

In this case the sector is represented by ROQ and the integration is therefore taken over the figure R_1R_2NKL. For in this area

$$\gamma\leqslant x\sin\theta/\cosh q\leqslant\delta.$$

Further, for this range of values $f(x)$ is zero. Therefore we have the identity

$$C=x\int\frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\,dq\int\frac{f(x\sin\theta/\cosh q)}{(\cos\theta)^{2\sigma-1}}\,d\theta,$$

where the integration is taken over the pentagon R_1R_2NKL.

Now, taking these integrations by means of strips parallel to the a-axis we have

$$C=x\int_0^{\cosh^{-1}(x/\gamma)}\frac{(\sinh q)^{2\sigma-1}dq}{\cosh^2 q}\int_0^{\sin^{-1}(\gamma\cosh q/x)}\frac{f(x\sin\theta/\cosh q)}{(\cos\theta)^{2\sigma-1}}\,d\theta$$

$$+x\int_{\cosh^{-1}(x/\gamma)}^\infty\frac{(\sinh q)^{2\sigma-1}dq}{\cosh^2 q}\int_0^{\pi/2}\frac{f(x\sin\theta/\cosh q)}{(\cos\theta)^{2\sigma-1}}\,d\theta$$

$$=\int_\gamma^x\frac{y\,dy}{(x^2-y^2)^{1-\sigma}}\int_0^y\frac{f(z)\,dz}{(y^2-z^2)^\sigma}+\int_0^\gamma\frac{y\,dy}{(x^2-y^2)^{1-\sigma}}\int_0^y\frac{f(z)\,dz}{(y^2-z^2)^\sigma},$$

writing as before,

$$\cosh q=x/y,\qquad\sin\theta=z/y.$$

To find C which depends only on γ and δ but is independent of x we make x tend to γ. Then

$$C=\operatorname*{lt}_{x\to\gamma}\int_0^\gamma\frac{y\,dy}{(x^2-y^2)^{1-\sigma}}\int_0^y\frac{f(z)\,dz}{(y^2-z^2)^\sigma},$$

and as before we have

$$\frac{\partial}{\partial\gamma}\mathrm{C}(\gamma,\delta)=\frac{\pi}{2\sin\sigma\pi}f(\delta),$$

and since C is certainly zero if γ is zero, we have

$$\mathrm{C}=\frac{\pi}{z\sin\sigma\pi}\int_0^{\gamma}f(t)\,dt.$$

Thus we have the identity

$$\int_{\gamma}^{x}\frac{y\,dy}{(x^2-y^2)^{1-\sigma}}\int_0^{y}\frac{f(z)\,dz}{(y^2-z^2)^{\sigma}}+\int_0^{\gamma}\frac{y\,dy}{(x^2-y^2)^{1-\sigma}}\int_0^{y}\frac{f(z)\,dz}{(y^2-z^2)^{\sigma}}$$
$$=\frac{\pi}{z\sin\sigma\pi}\int_0^{\gamma}f(z)\,dz, \qquad \ldots \quad (44)$$

which is true when $x>y$, for almost all arbitrary functions f.

It is also possible as in (37) to carry out the integrations by means of strips parallel to the b-axis. Then we find

$$\mathrm{C}=x\int_0^{\sin^{-1}(\gamma/x)}\frac{d\theta}{(\cos\theta)^{2\sigma-1}}\int_0^{\infty}\frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\,dq\,f(x\sin\theta/\cosh q)$$
$$+x\int_{\sin^{-1}(\gamma/x)}^{\pi/2}\frac{d\theta}{(\cos\theta)^{2\sigma-1}}\int_{\cosh^{-1}(x\sin\theta/\gamma)}^{\infty}\frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}dq$$
$$\times f(x\sin\theta/\cosh q).$$

And using as in (37) the substitutions

$$\lambda=x\sin\theta, \qquad \mu=\lambda/\cosh q,$$

we obtain

$$\mathrm{C}=x^{2\sigma}\int_0^{\gamma}\frac{d\lambda/\lambda}{(x^2-\lambda^2)^{\sigma}}\int_0^{\lambda}\frac{\mu^{2-2\sigma}f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}}$$
$$+x^{2\sigma}\int_{\gamma}^{x}\frac{d\lambda/\lambda}{(x^2-\lambda^2)^{\sigma}}\int_0^{\gamma}\frac{\mu^{2-2\sigma}f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}}.$$

To find C, we again make x tend to γ. Then we have

$$\mathrm{C}=\operatorname*{lt}_{x\to\gamma}x^{2\sigma}\int_0^{\gamma}\frac{d\lambda/\lambda}{(x^2-\lambda^2)^{\sigma}}\int_0^{\lambda}\frac{\mu^{2-2\sigma}f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}},$$

and using the value as before for $x=\gamma$ we get

$$\frac{\partial\mathrm{C}}{\partial\gamma}=\frac{\pi}{2\sin\sigma\pi}f(\gamma),$$

and therefore

$$C = \frac{\pi}{2 \sin \sigma\pi} \int_0^\gamma f(\mu)\, d\mu,$$

C evidently being zero when $\gamma = 0$. Thus our identity above may be written

$$x^{2\sigma} \left\{ \int_0^\gamma \frac{d\lambda/\lambda}{(x^2-\lambda^2)^\sigma} \int_0^\lambda \frac{\mu^{2-2\sigma} f(\mu)\, d\mu}{(\lambda^2-\mu^2)^{1-\sigma}} + \int_\gamma^x \frac{d\lambda/\lambda}{(x^2-\lambda^2)^\sigma} \int_0^\gamma \frac{\mu^{2-2\sigma} f(\mu)\, d\mu}{(\lambda^2-\mu^2)^{1-\sigma}} \right\} = \frac{\pi}{2 \sin \sigma\pi} \int_0^\gamma f(\mu)\, d\mu. \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

It remains to discuss the case when x is greater than δ and *a fortiori* greater than γ.

Case 3 *D*. $\gamma < \delta < x$.

In this case the sector bounded by the lines

$$\frac{a}{b} = \frac{\gamma}{x}, \quad \frac{a}{b} = \frac{\delta}{x}$$

may be represented by ROS. The area belonging to the rectangle

$$a = 0, \quad b = 1, \quad a = 1, \quad b = \infty,$$

namely the rectangle KLMN, which lies outside the sector, consists of two parts, the triangle R_1MR_2 and the pentagon S_1S_2NKL. And it is over these two distinct areas that the integration in this case must be performed.

Taking strips parallel to the a-axis we have for the integration over R_1MR_2

$$x \iint_{R_1MR_2} \frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\, dq \frac{f(x \sin\theta/\cosh q)}{(\cos\theta)^{2\sigma-1}}\, d\theta = \int_\delta^x \frac{y\, dy}{(x^2-y^2)^{1-\sigma}} \int_\delta^y \frac{f(z)\, dz}{(y^2-z^2)^\sigma}.$$

Further, again taking strips parallel to the a-axis we have for the integration over S_1S_2NKL,

$$x \iint_{S_1S_2NKL} \frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q}\, dq \frac{f(x \sin\theta/\cosh q)}{(\cos\theta)^{2\sigma-1}}\, d\theta = \int_\gamma^x \frac{y\, dy}{(x^2-y^2)^{1-\sigma}} \int_0^y \frac{f(z)\, dz}{(y^2-z^2)^\sigma} + \int_0^\gamma \frac{y\, dy}{(x^2-y^2)^{1-\sigma}} \int_0^y \frac{f(z)\, dz}{(y^2-z^2)^\sigma}.$$

Thus the theorem stands in the form :—

If $\gamma < \delta < x$, then

$$f(x) = \frac{2}{\pi} \sin \sigma\pi \frac{\partial}{\partial x} \left\{ \int_\delta^x \frac{y\,dy}{(x^2-y^2)^{1-\sigma}} \int_\delta^y \frac{f(z)\,dz}{(y^2-z^2)^\sigma} + \int_\gamma^x \frac{y\,dy}{(x^2-y^2)^{1-\sigma}} \int_0^y \frac{f(z)\,dz}{(y^2-z^2)^\sigma} + \int_0^\gamma \frac{y\,dy}{(x^2-y^2)^{1-\sigma}} \int_0^y \frac{f(z)\,dz}{(y^2-z^2)^\sigma} \right\} \quad . \quad . \quad (46)$$

This is also a result of very considerable generality.

Finally, if these integrations were performed by means of strips parallel to the b-axis, we should arrive by analogy with (43) at the result :

If $\gamma < \delta < x$, then

$$f(x) = \frac{2}{\pi} \sin \sigma\pi \frac{\partial}{\partial x} \cdot x^{2\sigma} \left\{ \int_\delta^x \frac{d\lambda/\lambda}{(x^2-\lambda^2)^\sigma} \int_\delta^\lambda \frac{\mu^{2-2\sigma} f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}} + \int_0^\gamma \frac{d\lambda/\lambda}{(x^2-\lambda^2)^\sigma} \int_0^\lambda \frac{\mu^{2-2\sigma} f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}} + \int_\gamma^x \frac{d\lambda/\lambda}{(x^2-\lambda^2)^\sigma} \int_0^\gamma \frac{\mu^{2-2\sigma} f(\mu)\,d\mu}{(\lambda^2-\mu^2)^{1-\sigma}} \right\} . \quad (47)$$

an alternative form of the same theorem.

The Application of Theorem B to a function which is zero for parts of its range.

The foregoing results consisting of integral equations and identities have been derived from the fundamental theorem

$$(A) \qquad f(x) = \frac{2}{\pi} \sin \sigma\pi \frac{\partial}{\partial x} \cdot x \int_0^\infty \frac{(\sinh q)^{2\sigma-1}}{\cosh^2 q} dq \times \int_0^{\pi/2} \frac{f(x \sin\theta/\cosh q)}{(\cos\theta)^{2\sigma-1}} d\theta,$$

which was itself derived from Fourier's sine formula,—where $f(x)$ can be zero for certain ranges of x.

Now the structurally related theorem—which has been derived from Fourier's cosine formula— is as follows :

$$(B) \qquad f(x) = -\frac{2}{\pi} \sin \sigma\pi \frac{\partial}{\partial x} \cdot x \int_0^{\pi/2} \frac{(\cos\theta)^{1-2\sigma}}{\sin^2\theta} d\theta \times \int_0^\infty \frac{f(x \cosh q/\sin\theta)}{(\sinh q)^{1-2\sigma}} dq,$$

—again with possible zero ranges for f.

It is evident that we may apply this theorem to a function $f(x)$ which is zero for values of x greater than δ and less than γ, provided that we integrate the right-hand side over values of θ and q such that

$$\gamma < x \cosh q/\sin\theta < \delta$$

and

$$0<\theta<\pi/2, \quad 0<q<\infty .$$

In fact, using again the substitutions

$$a=\sin\theta, \quad b=\cosh q,$$

integrations have to be performed over the area common to the rectangle

$$a=0, \quad a=1, \quad b=1, \quad b=\infty ,$$

and the sector bounded by the lines

$$a/b=x/\gamma, \quad a/b=x/\delta.$$

Case 1 *E*. $x>\delta>\gamma$.

Taking the various cases in order we find that when $x>\delta>\gamma$ so that the sector is bounded by two lines for which $a/b>1$, there is no area common to the rectangle KLMN and the sector, which in this case may be represented by POQ. Thus we merely find that $f(x)$ is zero when $x>\delta>\gamma$, as would be anticipated. It will be remarked that there is a close relationship between this case and case 1 C.

Case 2 *E*. $\delta>x>\gamma$.

In this case, which closely resembles case 2 C, the line OQ represents the line

$$a/b = x/\delta,$$

and OR the line

$$r/b = x/\delta,$$

so that the area over which the integration has to be performed is the triangle R_1MR_2. Thus we find

$$-\frac{\pi}{2\sin\sigma\pi}f(x)=\frac{\partial}{\partial x}\cdot x\int_0^{\cosh^{-1}\delta/x}(\sinh q)^{2\sigma-1}\,dq \times\int_{\sin^{-1}(x\cosh q/\delta)}^{\pi/2}\frac{f(x\cosh q/\sin\theta)}{\sin^2\theta(\cos\theta)^{2\sigma-1}}\,d\theta,$$

and with the substitutions

$$\cosh q=\lambda/x, \quad \sin\theta=\lambda/\mu,$$

it becomes

$$-\frac{\pi}{2\sin\sigma\pi}f(x)=\frac{\partial}{\partial x}\cdot x\int_x^\delta\frac{d\lambda/x}{(\lambda^2/x^2-1)^{1-\sigma}}\int_\lambda^\delta\frac{f(\mu)\,d\mu/\lambda}{(1-\lambda^2/\mu^2)^\sigma}$$

$$=\frac{\partial}{\partial x}\cdot x^{2-2\sigma}\int_x^\delta\frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_\lambda^\delta\frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^\sigma},\quad(48)$$

or with

$$x^2=s,\quad \lambda^2=t,\quad \mu^2=u,\quad \delta^2=\rho,\quad f(x)/x=\phi(s),$$

$$-\frac{\pi}{\sin\sigma\pi}\phi(s)=\frac{\partial}{\partial s}\cdot s^{1-\sigma}\int_s^\rho\frac{dt/t}{(t-s)^{1-\sigma}}\int_t^\rho\frac{u^\sigma\phi(u)\,du}{(u-t)^\sigma},\ \text{if } \rho>s.$$

. . . (49)

Alternatively, if we carry out the integration by means of strips parallel to the b-axis, we find

$$-\frac{\pi}{2\sin\sigma\pi}f(x)=\frac{\partial}{\partial x}\cdot x\int_{\sin^{-1}(x/\delta)}^{\pi/2}\frac{d\theta}{(\cos\theta)^{2\sigma-1}\sin^2\theta}$$

$$\times\int_0^{\cosh^{-1}(\delta\sin\theta/x)}\frac{f(x\cosh q/\sin\theta)\,dq}{(\sinh q)^{1-2\sigma}},$$

and writing as before

$$\sin\theta=x/y,\quad \cosh q=z/y,$$

we deduce, for $x<\delta$

$$-\frac{\pi}{2\sin\sigma\pi}f(x)=\frac{\partial}{\partial x}\cdot x\int_x^\delta\frac{dy/x}{(1-x^2/y^2)^\sigma}\int_y^\delta\frac{f(z)\,dz/y}{(z^2/y^2-1)^{1-\sigma}}$$

$$=\frac{\partial}{\partial x}\int_x^\delta\frac{y\,dy}{(y^2-x^2)^\sigma}\int_y^\delta\frac{f(z)\,dz}{(z^2-y^2)^{1-\sigma}},\quad . \quad . \quad (50)$$

or with

$$x^2=\xi,\quad y^2=\eta,\quad z^2=\zeta,\quad \gamma^2=\nu,\quad f(x)/x=\phi(\xi),$$

$$-\frac{\pi}{\sin\sigma\pi}\phi(\xi)=\frac{\partial}{\partial\xi}\int_\xi^\nu\frac{d\eta}{(\eta-\xi)^\sigma}\int_\eta^\nu\frac{\phi(\zeta)\,d\zeta}{(\zeta-\eta)^{1-\sigma}}.\quad . \quad (51)$$

Thus we have from (48, 49) the following integral relations or inversion formulæ :—

(*a*) If

$$h(\lambda)=\int_\lambda^\delta\frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^\sigma},$$

then

$$f(x)=-\frac{2\sin\sigma\pi}{\pi}\frac{\partial}{\partial x}\cdot x^{2-2\sigma}\int_x^\delta\frac{h(\lambda)\,d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}:\quad . \quad (52)$$

and

(*b*) If

$$\theta(t)=\int_t^\rho \frac{u^\sigma \phi(u)\,du}{(u-t)^\sigma},$$

then

$$\phi(s)=-\frac{\sin\sigma\pi}{\pi}\frac{\partial}{\partial s}\cdot s^{1-\sigma}\int_s^\rho \frac{\theta(t)\,dt/t}{(t-s)^{1-\sigma}}. \quad . \quad . \quad . \quad (53)$$

Similarly from (50, 51) we deduce the inversion formulæ:

(*c*) If

$$g(y)=\int_y^\delta \frac{f(z)\,dz}{(z^2-y^2)^{1-\sigma}},$$

then

$$f(x)=-\frac{2\sin\sigma\pi}{\pi}\frac{\partial}{\partial x}\int_x^\delta \frac{y\,g(y)\,dy}{(y^2-x^2)^\sigma}: \quad . \quad . \quad (54)$$

and

(*d*) If

$$\chi(\eta)=\int_\eta^\nu \frac{\phi(\xi)\,d\xi}{(\xi-\eta)^{1-\sigma}},$$

then

$$\phi(\xi)=-\frac{\sin\sigma\pi}{\pi}\frac{\partial}{\partial\xi}\int_\xi^\nu \frac{\chi(\eta)\,d\eta}{(\eta-\xi)^\sigma}. \quad . \quad . \quad . \quad (55)$$

A particular case is of special importance, namely the case $\sigma=\frac{1}{2}$. Then

$$f(x)=-\frac{2}{\pi}\int_x^\delta \frac{y\,dy}{(y^2-x^2)^{\frac{1}{2}}}\int_y^\delta \frac{f(z)\,dz}{(z^2-y^2)^{\frac{1}{2}}},$$

and if

$$g(y)=\int_y^\delta \frac{f(z)\,dz}{(z^2-y^2)^{\frac{1}{2}}},$$

then

$$f(x)=-\frac{2}{\pi}\frac{\partial}{\partial x}\int_x^\delta \frac{y\,g(y)\,dy}{(y^2-x^2)^{\frac{1}{2}}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

This is the Bateman-Herglotz equation already mentioned. The other form of these theorems gives

$$f(x)=-\frac{2}{\pi}\frac{\partial}{\partial x}\cdot x\int_x^\delta \frac{d\lambda/\lambda}{(\lambda^2-x^2)^{\frac{1}{2}}}\int_\lambda^\delta \frac{\mu f(\mu)\,d\mu}{(\mu^2-\lambda^2)^{\frac{1}{2}}}, \quad . \quad (57)$$

and if

$$h(\lambda)=\int_\lambda^\delta \frac{\mu f(\mu)\,d\mu}{(\mu^2-\lambda^2)^{\frac{1}{2}}},$$

then

$$f(x)=-\frac{2}{\pi}\frac{\partial}{\partial x}\cdot x\int_x^\delta \frac{h(\lambda)\,d\lambda/\lambda}{(\lambda^2-x^2)^{\frac{1}{2}}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

In another form the latter formula becomes the degenerate case $\delta = \infty$:—

If

$$h(\lambda) = \int_0^\infty \lambda \cosh u f(\lambda \cosh u)\, du,$$

then

$$f(x) = -\frac{2}{\pi}\frac{\partial}{\partial x}\cdot\int_0^\infty h(x\cosh v)\, dv/\cosh v, \quad . \quad (59)$$

—an equation discussed by Lamb in relation to hydrodynamics.

As an interesting illustration we take

$$h(\lambda) = \lambda J_0(2\lambda),$$

and we find

$$f(x) = -\frac{2}{\pi}\frac{\partial}{\partial x}\cdot x\int_0^\infty J_0(2x\cosh v)\, dv$$

$$= \frac{1}{\pi}\frac{\partial}{\partial x}\cdot x\, J_0(x)\, Y_0(x)$$

by a well-known formula. Thus

$$J_0(2\lambda) = \frac{1}{\pi}\int_0^\infty \cosh u \frac{\partial}{\partial \lambda}\cdot\{\lambda J_0(\lambda\cosh u)\, Y_0(\lambda\cosh u)\}\, du$$

$$= \frac{1}{\pi}\frac{\partial}{\partial \lambda}\cdot\lambda\int_1^\infty \frac{J_0(\lambda t)\, Y_0(\lambda t)\, t\, dt}{(t^2-1)^{\frac{1}{2}}}, \quad . \quad . \quad . \quad . \quad (60)$$

a formula of a type which is difficult to prove otherwise.

We have, lastly, to discuss the case when x is less than γ and *a fortiori* less than δ.

Case 3 E. $\delta > \gamma > x$.

In this case the lines

$$a/b = x/\gamma, \quad a/b = x/\delta$$

may be represented by OR and OS and the area over which the integration has to be performed is therefore represented by $R_1R_2S_2S_1$. Thus taking strips parallel to the a-axis

we find that

$$-\frac{\pi}{2\sin\sigma\pi}f(x)=\frac{\partial}{\partial x}\cdot x\int_0^{\cosh^{-1}\gamma/x}(\sinh q)^{2\sigma-1}\,dq \times\int_{\sin^{-1}(x\cosh q/\gamma)}^{\sin^{-1}(x\cosh q/\delta)}\frac{f(x\cosh q/\sin\theta)}{\sin^2\theta\,(\cos\theta)^{2\sigma-1}}\,d\theta +\frac{\partial}{\partial x}\cdot x\int_{\cosh^{-1}\gamma/x}^{\cosh^{-1}\delta/x}(\sinh q)^{2\sigma-1}\,dq \times\int_{\sin^{-1}(x\cosh q/\delta)}^{\pi/2}\frac{f(x\cosh q/\sin\theta)}{\sin^2\theta\,(\cos\theta)^{2\sigma-1}}\,d\theta,$$

and with the substitutions

$$\cosh q=\lambda/x,\quad \sin\theta=\lambda/\mu,$$

this formula becomes

$$-\frac{\pi}{2\sin\sigma\pi}f(x)=\frac{\partial}{\partial x}\cdot x^{2-2\sigma}\int_x^{\gamma}\frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_{\gamma}^{\delta}\frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^{\sigma}} +\frac{\partial}{\partial x}\cdot x^{2-2\sigma}\int_{\gamma}^{\delta}\frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_{\lambda}^{\delta}\frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^{\sigma}}.$$

But when $x<\gamma$, $f(x)=0$. Hence we arrive at an identity

$$x^{2-2\sigma}\left\{\int_x^{\gamma}\frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_{\gamma}^{\delta}\frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^{\sigma}} +\int_{\gamma}^{\delta}\frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_{\gamma}^{\delta}\frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^{\sigma}}\right\}=C,$$

where C is independent of x.

To find C we may make x tend to γ. Then we have

$$C=\lim_{x\to\gamma}x^{2-2\sigma}\int_{\gamma}^{\delta}\frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_{\lambda}^{\delta}\frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^{\sigma}}.$$

Now by theorem (48) it follows that

$$\frac{\partial C}{\partial\gamma}=-\frac{\pi}{2\sin\sigma\pi}f(\gamma),$$

and therefore

$$C=-\frac{\pi}{2\sin\sigma\pi}\int_{\delta}^{\gamma}f(\mu)\,d\mu,$$

the lower limit being δ since $C=0$ when $\gamma=\delta$. Thus we

have the identity

$$x^{2-2\sigma}\left\{\int_x^\gamma \frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_\gamma^\delta \frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^\sigma} + \int_\gamma^\delta \frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_\lambda^\delta \frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^\sigma}\right\}$$
$$= -\frac{\pi}{2\sin\sigma\pi}\int_\delta^\gamma f(\mu)\,d\mu = \frac{\pi}{2\sin\sigma\pi}\int_\gamma^\delta f(\mu)\,d\mu. \quad (61)$$

This result has been obtained by integrating strips of the area $R_1R_2S_2S_1$ parallel to the a-axis. Just as in the case of the corresponding D-case we have an equivalent result of a different form for integration by means of strips parallel to the b-axis, namely

$$\int_x^\gamma \frac{y\,dy}{(y^2-x^2)^\sigma}\int_\gamma^\delta \frac{f(z)\,dz}{(z^2-y^2)^{1-\sigma}} + \int_\gamma^\delta \frac{y\,dy}{(y^2-x^2)^\sigma}\int_y^\delta \frac{f(z)\,dz}{(z^2-y^2)^{1-\sigma}}$$
$$= +\frac{\pi}{2\sin\pi\sigma}\int_\gamma^\delta f(z)\,dz. \quad (62)$$

We do not give a detailed proof of this theorem, since its truth is evident if we compare theorems (61) and (47) and theorem (46) with our final result.

This nearly completes the discussion of the application of the method to a function $f(x)$ which is zero for positive values of x greater than δ or less than γ.

To complete the scheme we have now to apply the theorem to a function $f(x)$ which is zero for values of x between γ and δ.

The detailed consideration of the various cases, when x is greater than δ, when it is between δ and γ, and when it is less than γ, can be left to the reader.

It will be sufficient to record the results.

Case 1 *F.* $x>\delta>\gamma$.

Thus when $x>\delta$, we shall obtain the original theorems

$$\frac{\pi}{2\sin\sigma\pi}f(x) = -\frac{\partial}{\partial x}\int_x^\infty \frac{y\,dy}{(y^2-x^2)^\sigma}\int_y^\infty \frac{f(z)\,dz}{(z^2-y^2)^{1-\sigma}}$$

$$\frac{\pi}{2\sin\sigma\pi}f(x) = -\frac{\partial}{\partial x}\cdot x^{2-2\sigma}\int_x^\infty \frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_\lambda^\infty \frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^\sigma}.$$

Case 2 *F.* $\delta > x > \gamma$.

Next when x lies between γ and δ, $f(x)$ is zero and we get an identity, namely

$$x^{2-2\sigma}\left\{\int_\delta^\infty \frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_\lambda^\infty \frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^\sigma} + \int_x^\delta \frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_\delta^\infty \frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^\sigma}\right\} = \frac{\pi}{2\sin\sigma\pi}\int_\delta^\infty f(\mu)\,d\mu \quad . \quad . \quad . \quad (63)$$

and the equivalent identity

$$\int_x^\delta \frac{y\,dy}{(y^2-x^2)^\sigma}\int_y^\infty \frac{f(z)\,dz}{(z^2-y^2)^{1-\sigma}} + \int_\delta^\infty \frac{y\,dy}{(\lambda^2-x^2)^\sigma}\int_y^\infty \frac{f(z)\,dz}{(z^2-x^2)^{1-\sigma}} = \frac{\pi}{2\sin\sigma\pi}\int_\delta^\infty f(z)\,dz. \quad . \quad (64)$$

Case 3 *F.* $\delta > \gamma > x$.

Then finally when x is less than γ and δ, we have the theorem

$$f(x) = -\frac{2}{\pi}\sin\sigma\pi\frac{\partial}{\partial x}\left\{\int_x^\gamma \frac{y\,dy}{(y^2-x^2)^\sigma}\int_y^\gamma \frac{f(z)\,dz}{(z^2-y^2)^{1-\sigma}} + \int_x^\delta \frac{y\,dy}{(y^2-x^2)^\sigma}\int_y^\infty \frac{f(z)\,dz}{(z^2-y^2)^{1-\sigma}} + \int_\delta^\infty \frac{y\,dy}{(y^2-x^2)^\sigma}\int_y^\infty \frac{f(z)\,dz}{(z^2-y^2)^{1-\sigma}}\right\}, \quad . \quad . \quad . \quad (65)$$

and the alternative form

$$f(x) = -\frac{2}{\pi}\sin\sigma\pi\frac{\partial}{\partial x}\cdot x^{2-2\sigma}\left\{\int_x^\gamma \frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_\lambda^\gamma \frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^\sigma} + \int_\delta^\infty \frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_\lambda^\infty \frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^\sigma} + \int_x^\delta \frac{d\lambda/\lambda}{(\lambda^2-x^2)^{1-\sigma}}\int_\delta^\infty \frac{\mu^{2\sigma}f(\mu)\,d\mu}{(\mu^2-\lambda^2)^\rho}\right\}. \quad . \quad . \quad . \quad . \quad . \quad (66)$$

This completes the inquiry into the deductions to be drawn from applying the fundamental theorem to a function of x which is zero from γ to δ. Some physical applications of these types of integral equation will be published later.

L. *Spectral Relationships of Lines arising from the Atoms of the First Row of the Periodic Table.* *By* R. A. Millikan *and* I. S. Bowen *.

I. *Spectra of Light Atoms in Many Stages of Stripping.*

OUR studies in the field of hot-spark vacuum spectrometry, combined with other work, have now led us to a practically complete understanding of all the radiations that can be emitted by the atoms of the first row of the periodic table in all stages of ionization of their valence electrons.

Thus (1) the complete spectrum of Li_I was already in the literature [1] before our work began.

(2) In the case of Be_I and Be_{II} a small number of lines had been identified by Back, but no term values obtained. We have now classified all the important lines having their origin in either of these two structures, and have obtained the corresponding term values [2].

(3) In the case of B_I [3], B_{II} [4], and B_{III} [5] we have identified all the strong lines of all these electronic forms and fixed the corresponding term values.

(4) In the case of carbon, Fowler had worked out most of the lines and term values of C_{II} [6]. We have completed C_{II} [3] and obtained the identification of all the important lines, and also worked out the term values of C_I [3], C_{III} [4], and C_{IV} [7]; so all of the important lines due to carbon are now classified.

(5) In the case of nitrogen, N_I has been worked out both as to lines and term values by Kiess [8] and Hopfield [9]. N_{II} was partially obtained by Fowler [10] and the analysis of the strong lines in the extreme ultra-violet was completed by Bowen [3]. Laporte [11], however, has called attention to the necessity of increasing Fowler's term values by about 20,000 frequency units. In N_{III}, Fowler has obtained the identification of five of the lines. The remaining nineteen lines were obtained by Bowen [3]. In N_{IV} [12] and N_V [13] we have identified a number of the important lines, but the remainder are so faint and fall so far down in the extreme ultra-violet that the corresponding term values have not been obtained.

(6) In the case of oxygen the O_I lines in the visible have long been known [14], and Hopfield [15] has extended into the ultra-violet the study of this spectrum. Also Fowler worked out the lines of O_{II} in the visible and near ultra-violet [16], and Bowen [3] has extended the identifications into

* Communicated by the Authors.

the extreme ultra-violet, and corrected errors in preceding term values. The important extreme ultra-violet lines of O_{III} and O_{IV} have been identified by Bowen [3], and tentative term values fixed. In O_V and O_{VI} we have identified a number of the important lines [17], but the remainder are unobtainable because faint and below 200 A.

(7) In the case of F_I, F_{II}, F_{III}, and F_{IV} a few visible lines have been identified by De Bruin [18], while the important ones in the extreme ultra-violet have been worked out by Bowen [3], but only tentative values fixed.

(8) In the case of Ne_I, Meissner and Paschen [19] obtained all the important lines and term values in the visible, and Lyman and Saunders [20] those in the ultra-violet.

II. *Regular and Irregular Doublet Laws.*

In the working out of the portions of the foregoing spectra for which we have been responsible, the older methods for the identification of lines have been supplemented by the use of new methods arising from the fact that we have been able to extend the most important X-ray laws into the field of optics [21]. Thus, by virtue of the high ionizing power of our hot sparks, we have been able to obtain for the first time in the field of optical spectra a long series of atoms of like electronic structure but of steadily progressing nuclear charge, such as Li_I, Be_{II}, B_{III}, C_{IV}, N_V, O_{VI}, and for this series we have found both of the X-ray laws known as the regular and the irregular doublet laws to hold.

The first of the foregoing laws states that the doublet separation should vary as the fourth power of the effective nuclear charge. It has enabled us to predict the doublet separations of lines to be identified.

The second, or irregular, doublet law has enabled us to predict the exact position in the spectrum of the line to be sought. Furthermore, this last law has not only done the most important service and been of constant use in predicting the position of new lines, but it has enabled us to determine at once the precise nature of the electron jumps involved in the production of unknown lines through the use of the relation which we pointed out as involved in it—*namely, that wherever the irregular doublet law holds, the corresponding electron jumps must always be between orbits of the same total quantum number* [12].

It was the discovery of these two laws in optics that enabled us to make a definite correlation between optical

and X-ray levels[21], and forced us definitely to the strange conclusion, published in 1924, that in addition to the relativity cause a non-relativistic cause of doublet separation must exist that yields a separation obeying exactly the relativity formula[22].

A cause satisfying this condition as well as the conditions imposed by Landé's work on the anomalous Zeeman effect was found a year later by Uhlenbeck and Goudsmit[23] in the spinning electron. This brilliant idea of the young Dutch physicists has already had extraordinary successes in correlating old phenomena and, in interpreting otherwise unexplained effects. It lies at the base of the physical interpretation of the new spectroscopic rules.

III. *The New Spectroscopic Rules.*

Since the very recent formulation by Russell[24], Pauli[25], Heisenberg[26], and Hund[27] of the new rules for the determination of the type of spectra arising from different electron configurations, we have found these new rules valuable adjuncts to the laws mentioned in Section II. in the classification of the more complex of our spectra. The detailed statement of these rules and their application to these spectra are given in the Appendix.

These rules were developed by Russell, Pauli, Heisenberg, and Hund from a study of calcium and the other elements of the third row, or the first long period, of the periodic table. The present work has shown that the types of spectra produced by the atoms of the first row of the periodic table are practically those demanded by these rules.

Again the empirical rule, formulated by Hund, that the separations are normal until a shell has become just half filled and then become inverted when more than half full, has been shown in this work to hold also for the elements of the first row. Thus all configurations having one or two p electrons are found here to have normal separations ; while with three electrons the separations become very small, and with four or five they widen out again, but with the order of their terms reversed—a behaviour which in Table I. we have represented by giving to the inverted separation a negative sign. In this table we have collected all the separations which have been obtained for the atoms of the first row in all stages of stripping (or ionization). The numbers at the extreme left of the first column represent the number of electrons in p orbits (from 1 up to 6) in the valence shell, *i. e.* the shell of total quantum number 2. The numbers at the tops of

TABLE I.—Fine-structure Separations in the Elements of the first row of the Periodic Table.

No. of p electrons.		No. of s electrons. 0.	1.	2.	3.
1	Li	^2P ·338	^3P	^2P	^3P
	Be	6·61	2·36 ·67		
	B	34·4		15·3	
	C	107·4	56·5 22·9	63·1	40·0
	N	259·1	143·8 61·7	174·2	136·36
	O	533·8	305·9 134·9	389	
			^1P		^1P
2	Be	^3P 2·03 1·41	^4P	^3P	^4P
	B				
	C	47·4 29·7	28·6 21·5	27·7 16	
	N	124·5 72·8	80·5 60·3	82·7 48·8	46·71
	O	268·2 155·4	185 132	192 116	158·52
	F			394 243	
			^2P		^2P
	C		41·6		
	N		110·8		83·12
	O		246		179·99
	B	^1D	^2D < 1	^1D	^2D
	C		$-$ 2·3		
	N		$-$ 5·9		
	O		$-10·9$		
		^1S	^2S	^1S	^2S
3		^4S	^5S	S	^5S
			^3S		^3S
	C	^2D	^3D $-$ 1·9 <1	^2D	^3D
	N		$-13·7$ <1	< 3	
	O		$-27·8$ <3	-18	
	F			-27	
			^1D		^1D
	C	^2P	^3P <1 <1	^2P	^3P
	N	6·9	<3 $-$ 6·5	< 3	
	O	10	<5 $-16·3$	-10	
			^1P		^1P
4	N	^3P	^4P $-$ 44·1 $-18·6$	^3P	^4P
	O		$-163·4$ $-82·1$	-158 $-$ 68	
	F		-342 -177	-344 -150	$-274·6$
			^2P -168		^2P
	O		-384		$-325·6$
	F				
	O	^1D	^2D -4	^1D	^2D
		^1S	^2S	^1S	^2S
5	F	^2P	^3P -301 -185	^2P -407	^3P
	Ne		^1P		$-417·45$
					^1P
6		^1S	S	^1S	^2S

the columns represent the number of valence electrons in *s* orbits. That this row shows in the fourth column three electrons in *s* orbits when there are only two ground *s* electrons, means that two electrons are in the two 2*s* orbits and one in a 3*s* orbit. *It will be seen from glancing down the table that for all the columns*, i. e. *for all possible numbers of* s *electrons, as soon as the number of* p *electrons has passed three, the separations have the negative sign*, i. e. *the terms have become inverted.*

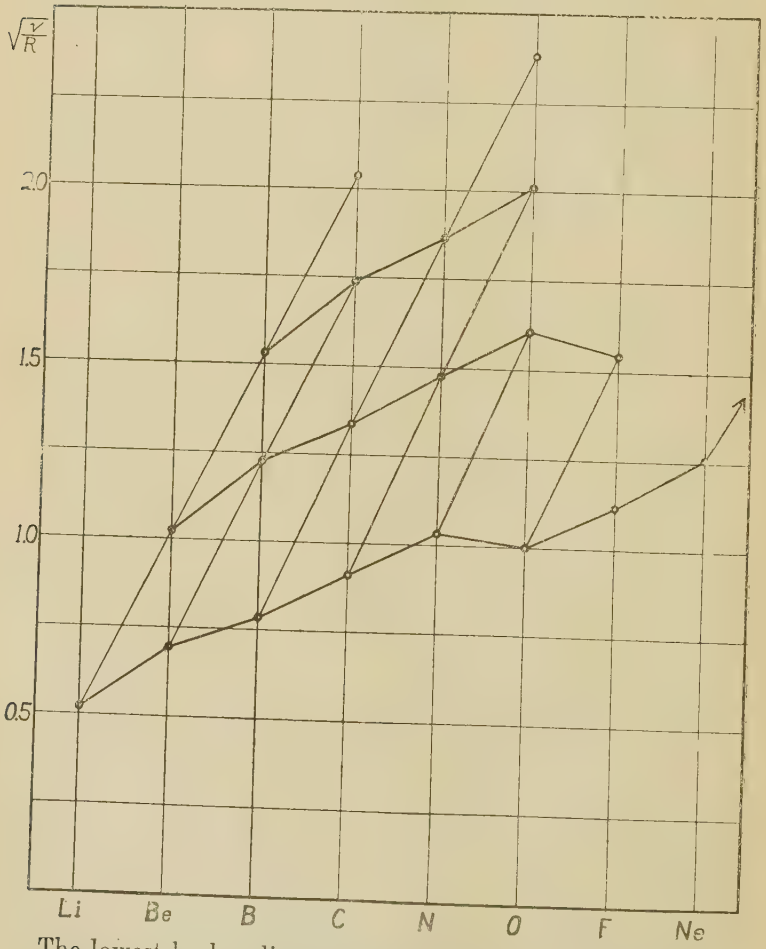
The fact that some squares contain two columns means that the particular configurations involved give rise to either triplet or quartet *p* terms, which of course have two characteristic separations. The type of the terms is indicated by the symbols at the extreme left within each square.

IV. *The Completed Moseley Diagram in the Field of Optics.*

In preceding papers we have shown that the Moseley law $\sqrt{\frac{\nu}{R}}=k(Z-\sigma)$ holds in the field of optics as well as in that of X-rays. This law in Moseley's hands represented merely a linear relation between atomic number Z and the square root of the frequency of a series of *corresponding lines,* and in our first paper [28] in this field we attempted to follow Moseley in plotting the relation between Z and what we thought to be a series of corresponding lines in our extreme ultra-violet spectra. More recently it has become customary, in presenting "Moseley straight lines" in the field of X-rays, to plot the relation between Z and the square root of the frequency corresponding to an *energy level, or term*, rather than to a line. Also in all of our own recent proofs of the validity of the Moseley law in the field of optics, it has been a linear relation between the square root of the frequencies of a series of corresponding levels and atomic number that we have exhibited. Indeed, *by this sort of plotting we have been able to show quite generally that a series of atoms of like electronic structure but varying charge always leads to a Moseley straight line.* This result is exhibited very beautifully in the diagram of fig. 1, in which the levels plotted – a small fraction of those we might plot—represent in every case the energy necessary to remove an electron from a *p* orbit of each of the atoms under consideration. The straight line farthest to the left represents the Moseley diagram for a one-valence electron system of this sort, the next line towards the right the same diagram for a two-electron system of this sort, the next that for a three-valence electron system, the next that

for a four-valence electron system, and so forth. The linear relations here shown are so perfect that the ionizing potentials can be quite accurately obtained for atoms for which they have not yet been determined, and that by simple extrapolation along these lines.

Fig. 1.



The lowest broken line running across the straight lines represents the series of energies necessary to remove an electron from the lowest p orbit in the case of a neutral atom, the next higher broken line the series of energies necessary to remove an electron from the lowest p orbit of a singly-ionized atom, and the broken line above that the series of

energies necessary to remove an electron from the lowest p orbit of a doubly-ionized atom. It is, of course, because these lines do not connect atoms of like electronic structure that they are broken instead of straight.

If the Moseley progression be defined as the progression exhibited by the square root of the energy of binding ($\sqrt{V}$) of a two-p electron by all the neutral atoms from hydrogen up to uranium, then the lower broken line of the chart depicts this progression up to neon, while from neon to uranium it is a practically straight line following the direction indicated by the arrow shown at the right side of this figure.

V. *Ionizing Potentials.*

The ionization potentials—the energy necessary to remove the most lightly bound electron—of all the atoms of the first row in all the degrees of stripping in which it has as yet been possible to obtain the limit of the appropriate series are collected in Table II. Some of these, notably those of

TABLE II.—Ionization Potentials.

	I.	II.	III.	IV.
Li.....	5·371			
Be	9·50	18·141		
B	8·34	24·2	37·786	
C	11·3	24·289	45·5 (*45*)	64·23
N	14·494	29·56 (*24*)	47·2 (*45*)	
O	13·565	34·999 (*32*)	54·8 (*45*)	77·0
F	16·9	32·3		
Ne	21·482			

carbon, nitrogen, and oxygen, are of much importance for fixing the temperatures of stars. Indeed, in some cases it has only been by working backwards from stellar temperatures estimated by other methods that rough estimates of these ionization potentials have heretofore been obtained. These previous estimates [29] are recorded in italics below the new values obtained from our spectroscopic measurements. The new values will be seen to be from one to twenty-five per cent. higher than the old.

Norman Bridge Laboratory of Physics,
California Institute of Technology,
Pasadena.

Appendix.

The Application of the New Spectroscopic Rules to the Spectra of the Atoms of the First Row of the Periodic Table.

The fundamental assumption underlying the modern quantum theory of spectra is that the moments of momentum of all rotary motions within the atom possess the fundamental quantum property of being able to change only by unit steps, *i. e.* all moments of momentum are quantized.

There are three different sorts of moments of momentum to consider. In the first instance, it is the moment of momentum of the individual electron in its orbit which has been quantized. The number of units in this orbital moment of momentum determines the so-called azimuthal quantum number of the orbit, and has heretofore been designated by the letter k.

When more than one electron is present within an atom, the total orbital moment of momentum of the whole group is obtained by taking the quantized vector sum of the individual orbital moments. But in this summation process, for reasons not yet fully understood, it is found necessary to reduce the previously assumed value of the azimuthal quantum number by unity. In order to avoid confusion, this new value of the azimuthal quantum number of each electron orbit is now designated by l, which means of course that $l=k-1$. Thus an s orbit has a value $l=0$, a p orbit $l=1$, a d orbit $l=2$, an f orbit $l=3$, etc.

The physical significance of the fact that the vector sum of the l's is quantized to obtain L is that the electrons are able to rotate only in orbits of such orientations about the nucleus that this vector sum is a whole number of units of moment of momentum.

In the second instance the moment of momentum of the spin of each electron on its axis is quantized. In order to obtain the following interpretations, it is found necessary to assume, first that the moment of momentum of spin of every individual electron within an atom is always one-half the fundamental unit of moment of momentum, *i. e.* it is $\frac{1}{2}\frac{h}{2\pi}$, and second that all electrons within an atom spin in the same plane, some however spinning in one direction and others in the exactly opposite sense. This last condition means that the total or resultant moment of momentum of spin of all the electrons within an atom is the algebraic sum of the spins of the individual electrons. This total spinning moment

of all the electrons of a given atom is designated by the letter R.

In the third instance, in order to obtain the total moment of momentum of the whole atom it is necessary to take the quantized vector sum of the orbital moments, L, and of the spin moment, R. This is precisely the quantity which was originally called by Sommerfeld the inner quantum number and designated by the letter J.

The fundamental quantum condition is now that all possible values of J constitute a series of which the successive steps differ by unity. If the value of R is an odd number of half units, *i. e.* if there are an odd number of spinning electrons, then all the values of J are found to be half integral ($\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, $3\frac{1}{2}$, etc.), while if the value of R is integral, then all the values of J are found to be likewise integral (1, 2, 3, etc.). The number of possible values of J obtained from a given pair of values of R and L gives the multiplicity, *i. e.* the number of terms in the fine structure. The maximum of the multiplicity is then $2R+1$.

The notation now in general use in the formulation of the new rules is as follows :—When the value of L built up as above from the vectorial summation of the *l*'s of the individual orbits is 0, the term is by definition an S term ; when $L=1$ the term is by definition a P term ; when $L=2$ it is a D term; when $L=3$ an F term, etc. The value of the maximum multiplicity, as determined by the above formula and involving only R, is indicated by a superscript preceding the letter. Thus doublet S, triplet P, etc. are written ^2S, ^3P, etc. When it is necessary to differentiate between the different P terms, for example, the value of J corresponding to each P term is written as a subscript, thus : $^2P_1$, $^3P_2$, etc. ; but for convenience in case of half-integral values of J it has been decided to use the next higher whole number, thus avoiding using fractional subscripts in the mere naming of the two P terms in a doublet, for example.

The word "configuration" will here be used to indicate the number of electrons in each of the different sorts of orbits. Thus s^2p^3 means a configuration of two electrons in *s* orbits and three electrons in *p* orbits, while $s^2p^2 \cdot p$ indicates the configuration in which one of the *p* electrons has been pushed up into a *p* orbit of higher total quantum number.

The foregoing quantization rules predict a much larger number of terms than are actually obtained from a given configuration ; and Pauli has formulated an exclusion rule which has a very illuminating physical significance, and

which succeeds in reducing the number of terms to those really observed. It is stated as follows :—No two electrons can be alike in all four of the quantum numbers necessary to describe their motions. These are, namely : (1) total quantum number (n), or *size of orbit* ; (2) azimuthal quantum number (k), or *shape of orbit* ; (3) projection of orbital moment of momentum upon a fixed direction of reference, or *orientation of orbit* ; (4) projection of moment of momentum of spin upon the fixed direction of reference, or *orientation of spin*. These last two are usually called magnetic quantum numbers, since the fixed direction is usually taken as that of a magnetic field, and must be so taken in the analysis of the Zeeman effects.

We shall now apply these rules to the interpretation of the spectra of the simpler atoms.

1. *Stripped Atoms, or One-electron Systems.*

In the case of the first atom, Li, of the first row the single outer or valence electron may be either in an elliptical orbit 2_1 or a circular orbit 2_2. In the latter case the orbit is in all of its parts far outside the inner pair of K electrons, so that the effective nuclear charge is very close to $3-2=1$, while in the case of the 2_1 orbit the approach to the nucleus at perihelion is very much closer, and hence the screening of the two K electrons much less perfect. The average binding of the electron in the 2_1 orbit is therefore much greater than that of the electron in the 2_2 orbit, so that the electron jump from the 2_2 to the 2_1 orbit gives rise to the familiar strong line of Li at 6708 A. The fact that this line is a doublet means that there are two circular (2_2) orbits, P_1, P_2, of slightly different energies, from which the electron may jump into the S or 2_1 orbit. The existence of just two levels is seen to be required by the foregoing rules, since by them $l=1$ and, since there is but one electron, $L=1$, and also $R=\frac{1}{2}$, so that J can have just two values, $\frac{1}{2}$ or $1\frac{1}{2}$, depending upon whether the two moments of momentum are added parallel or antiparallel. The theory of the spinning electron thus accounts for the difference in energy of these two orbits merely by the assumption that in one case the electron is spinning in the direction of the orbit, and in the other case in the opposite direction. The foregoing set of rules accounts for the fact that while there are two P levels there is but one S level, since for this level l equals 0, and hence $L=0$, and this can be combined with $R=\frac{1}{2}$ only so as to yield one value of the total moment of momentum J of the atom, viz. $J=\frac{1}{2}$.

The spectra of all the stripped atoms Li_{II}, Be_{II}, B_{III}, C_{IV}, N_V, O_{VI}, F_{VII} are of the same type as that of Li, and in our work with them the new rules have not been used, the older methods (Rydberg-Ritz formula) and the regular and irregular doublet laws being sufficient for all identifications.

2. *Two-electron Systems.*

In the case of the second atom of the row, viz. Be, there are two valence electrons which in the normal or ground state must both be in 2_1, *i. e.* in *s* orbits. We shall consider first a configuration in which one of these two *s* electrons has been moved out to some more remote orbit, such as a *p* orbit. Here the *l*'s to be summed vectorially are $l=0$ and $l=1$. Hence $L=1$, also $R=\frac{1}{2}+\frac{1}{2}=1$, or $\frac{1}{2}-\frac{1}{2}=0$. The quantized vector sum of $L=1$ and $R=1$ is $J=0$, 1, or 2. This is therefore a triplet level, while when $L=1$ and $R=0$, $J=1$. This is therefore a singlet level. This configuration therefore gives rise to triplet or singlet levels and since $L=1$ to triplet P terms (^3P) or singlet P terms (^1P).

If the excited electron had gone to a *d* orbit (3_3, 4_3, 5_3, etc.), then for the two orbits $l=0$ and $l=2$; therefore $L=2$, while, as above, $R=1$ or 0. This gives either $J=1$, 2, 3 or $J=2$, *i. e.*, as above, it gives rise to triplet or singlet D terms (^3D or ^1D).

Similarly there always result singlet or triplet terms for all positions of one electron, since for the other electron $l=0$ and the type of the term is the same as the type of the orbit of the excited electron.

When the atom has settled down to its ground state, *i. e.* when both electrons are in the two *s* orbits, both *l*'s are 0, hence $L=0$. Also, so far as the foregoing rules go, $R=\frac{1}{2}+\frac{1}{2}=1$, or $\frac{1}{2}-\frac{1}{2}=0$, and hence $J=1$ or 0; but this leads to a predicted number of levels which in the case of two $2s$ orbits is never found in practice, since they are excluded by the Pauli rule, which in this case means that, since the $2s$ electrons have orbits of the same (1) size, (2) shape, and (3) orientation, they cannot be spinning in the same direction, so that $R=\frac{1}{2}-\frac{1}{2}=0$. Hence, since $L=0$, $J=0$, this means that the moment of momentum of the atom equals 0; and this requires a singlet term since the maximum possible multiplicity is the number of possible values of J, which is here 1.

It will be seen from exactly the same sort of analysis that the Pauli rule requires that the moment of momentum of the K shell is always 0. Similarly it actually always requires

that the moment of momentum of any closed shell is 0; and this means, of course, that it is only the electrons in partially-filled shells which determine the moment of momentum of the atom.

There is another configuration of the two electrons of Be which is of interest in connexion with the Pauli rule, namely when one excited electron has moved up to some higher s orbit. Then, since the two orbits now differ in size, though they are alike in shape, both being s orbits, they may be alike in both orientation and spin, so that $R=1$ or 0, and hence any pair of values of L and R, viz. $L=0$ and $R=1$, or $L=0$ and $R=0$, can give rise only to a single term. In general, however, for all values of L other than its zero value, there result from the quantized vector addition of any of these values with the value $R=1$ three possible values of J, viz. $L+1$, L, and $L-1$, and when L is thus combined with $R=0$, one possible value of J, viz. L. It is then found convenient to classify all terms resulting from $R=1$ as belonging to the triplet system, and all resulting from $R=0$ as belonging to the single system. This notation makes it possible to set up the foregoing general rule, which makes term multiplicity independent of L and dependent upon R alone as stated. The *tour de force* by which this rule has been arrived (ignoring the value $L=0$) finds some physical justification in the fact that combinations (electron jumps) do actually occur most strongly between terms having the same value of R, whether $L=0$ or $L>0$, so that the particular single term arising from $L=0$, $R=1$ does actually belong with the triplet system. With this explanation as to notation we may henceforth always determine maximum multiplicity with the foregoing formula, multiplicity $=2R+1$.

Another very interesting configuration is that in which both electrons have been raised into p orbits (the p^2 configuration). Here for each orbit $l=1$, therefore $L=0$, 1, or 2. Also $R=\frac{1}{2}+\frac{1}{2}=1$, or $\frac{1}{2}-\frac{1}{2}=0$. When $L=0$ we have by definition an S term, and when this value of L is combined with $R=0$, there results $J=0$, *i. e.* a singlet S term. When $L=0$ is combined with $R=1$, there results $J=1$, again a single term, which by the above rule, however, belongs to the triplet system, and hence is usually spoken of as a triplet S term. When the values $L=1$ or 2 are combined with $R=0$, there result $J=1$ or 2 respectively, *i. e.* a singlet P term or a singlet D term. And when the values $L=1$ or 2 are combined with $R=1$, there result triplet P or triplet D terms. In a word, then, this configuration gives rise only to singlet

and triplet terms. This might have been found at once from the foregoing rule, that the maximum multiplicity is given by $2R+1$.

Of the foregoing terms, all save the singlet S, triplet P, and singlet D terms are actually forbidden by the Pauli exclusion rule, as can be seen by working out, a rather tedious process, the possible combinations of the four quantum numbers for each of the two electrons in such a way as to always make at least one of the four different for the two electrons.

In the actual practice of spectroscopy none of the foregoing singlet terms have thus far been located. This is due to the fact that since there are in the case of singlet lines no characteristic frequency differences to search for, singlets are in general very difficult to identify.

The foregoing triplet P terms (P_0, P_1, P_2), which alone remain of the terms corresponding to the configuration of two electrons in p orbits, are actually identical with the three p' terms which we found combining strongly with the triplet P terms of the sp configuration to produce "the flag"—the pp' group—that we found to be characteristic of all two-electron systems formed from atoms of the first two rows of the periodic table; that is, all these pp' groups in two-electron systems of these elements are formed by the removal of both electrons to p orbits and the subsequent return of one of them to an s orbit. In the removal the two electrons may have three different orientations of the plane in which they are both spinning with respect to the L vector, and each of these orientations has a slightly different energy. Similarly, after the return of one of them the plane in which the two are now spinning may have three different orientations with respect to the new L vector. Were it not for the selection principle that J can change only by ± 1 or 0, the jump for the upper group of three states to the lower group of three might be made in nine different ways. The above selection principle reduces these nine to six, which then correspond to the six observed lines of "the flag."

We have now discussed all the levels in two-electron Be that are near enough to the ground-level to give rise to lines of an appreciable strength. The discussion of Be_I applies *in toto* to all the two-electron systems, B_{II}, C_{III}, N_{IV}, O_V, F_{VI}.

3. *Three-electron Systems.*

In the case of a three-electron system when two of them are in the ground state, *i.e.* in s orbits for precisely the same reasons stated on p. 572, the Pauli rule requires that these

two electrons spin in opposite directions. Further, the same rule precludes the third electron from being in a $2s$ state, since, if it were, this third s state would have to be identical with one of the other two. In other words, there can never be more than two electrons in an s state of a given total quantum number. This fact was first discovered by Stoner from a considerable amount of experimental data, and was then shown by Pauli to be a consequence of this rule. The ground state of a three-electron system is then two electrons in s orbits and one in a p orbit. But since, as in the case of the two electrons in the K shell, the value of the moment of momentum for these two electrons is zero, the moment of momentum of the atom is determined simply by the p electron. It follows that all the types of spectra possible with a three-electron system when the two s orbits are filled are the same as those of a one-electron system like Li, discussed above, save for the fact that the 2S term is missing because the $2s$ orbits are full. Here therefore, as in the alkalis, the terms are all doublets.

To take one particular three-electron system which is altogether typical of them all, consider N_{III}. One of the strongest lines to be expected involving the foregoing configuration of two electrons in s orbits and one in a p orbit—a s^2p configuration—is that produced by the jump from s^2d to s^2p. This corresponds to the combination of the doublet D of the s^2d configuration with the doublet P of the s^2p configuration (^{2}D of $s^2d \longrightarrow {}^2$P of s^2p). In N_{III} this is the strong line at 374 A. The next strongest line corresponds to the combination of the doublet S of the $s^2.s$ configuration (two electrons in the $2s$ state and one in an excited s state) with the doublet P of the s^2p configuration (^{2}S of $s^2.s \longrightarrow {}^2$P of s^2p). In N_{III} this is the strong doublet line at 452 A.

Nothing further need be said about the case in which the two $2s$ orbits are filled, although there are weaker lines corresponding to jumps of this single electron between excited states.

But when one of these $2s$ electrons has been pushed up into a p orbit, so that the configuration is one s electron and two p electrons, (sp^2) the two p electrons alone would give rise, as shown on p. 572, to singlet S, triplet P, and singlet D terms. Now a singlet S when combined with one s electron, having the value $l=0$ and $r=\frac{1}{2}$, produces $L=0$, $R=\frac{1}{2}$, which corresponds to doublet S terms (^{2}S). Again, a singlet D combined with one s electron produces $L=2$, $R=\frac{1}{2}$, which corresponds to doublet D terms (^{2}D). Finally,

triplet P terms when combined with one s electron produce $L=1$, $R=\frac{1}{2}$ or $1\frac{1}{2}$, which corresponds to doublet and quartet terms respectively (^2P and ^4P).

All of these doublet terms combine strongly with the doublet P term of the s^2p configuration. Thus the doublet D combining with the doublet P of the s^2p configuration gives rise to the pair at 991 A, which are the strongest lines in the whole N_{III} spectrum. Again, the doublet P of the sp^2 configuration combining with the P of the s^2p configuration gives rise to what we have called the pp' "flag" of the three-electron system at 686 A. Also the doublet S of the sp^2 configuration combining with the doublet P of the s^2p configuration gives rise to the pair of lines at 764 A.

Another configuration which is found to occur frequently is p^3, both of the two s electrons having been pushed up into p positions. Analysis similar to the foregoing shows, in view of the Pauli exclusion rule, that the following terms are possibilities: quartet S, doublet P, doublet D. The doublet P of this p^3 configuration combines strongly with the doublet P of the sp^2 configuration to produce the strong pair at 1184 A. It also combines with the doublet S and the doublet D to give rise to the lines at 1006 A and 773 A respectively. Also the quartet S of p^3 combines with the quartet P of sp^2 to give the strong group at 772 A.

This covers all of the configurations which take part in forming strong lines in N_{III}. Further, the foregoing analysis of course applies to all of the three-electron systems which can be formed from any of the atoms here under consideration: *i. e.* it applies to B_I, C_{II}, and O_{IV} as well as to N_{III}. Also, since all of the lines formed by the changes in the last two configurations above considered are changes in which the total quantum number of all electrons remain unaltered, these lines must all follow the irregular doublet law, a law which was actually a very important factor in their identification.

4. *Four-electron Systems.*

A typical four-electron system is N_{II}. The ground state is, of course, the s^2p^2 configuration. As shown above, the two s electrons have zero momentum; so that the types of terms are identical with those of two electrons in p orbits such as were discussed above under two-electron systems. As shown above (p. 572), this configuration gives rise to a singlet S, a singlet D, and a triplet P.

When one of the p electrons is pushed up into an excited s orbit ($s^2p.s$), the effect of the s^2 is zero, and hence the

type of the terms are those found with one electron in a p and one in an s orbit. These are, as shown above, a singlet P and a triplet P. The combination of this with the ground configuration gives rise to two singlets (not yet identified) and the pp' group of six lines at 672 A.

The $s^2p\,.\,p$ configuration gives terms of the same type as those we worked out for a two-electron system with both electrons in p orbits, save that in this case these two electrons are not in orbits of the same total quantum number, so that Pauli's exclusion rule no longer applies. Hence all the terms discussed on p. 572 are present, namely singlet S, P, D, and triplet S, P, D. This configuration, in passing over into $s^2p\,.\,s$, produces many lines in the visible (for the identification of which A. Fowler has been largely responsible), but none in the region of our activity.

The $s^2p\,.\,d$ configuration is unlike any as yet discussed. Its s^2 part can be ignored, thus leaving two orbits for which $l=1$ and $l=2$ respectively. These combine into L = 1, 2, or 3. Further, R = 0 or 1. The first value of R gives singlets and the last triplets, so that we have singlet P, singlet D, and singlet F terms, also triplet P, triplet D, and triplet F terms. Of all the combinations possible between these terms and those of the s^2p^2 configuration, only one has been found, namely from the triplet P of $s^2p\,.\,d$ to triplet P of s^2p^2. These are the very close lines at 534 A.

The sp^3 configuration is the p^3 discussed on p. 575 combined with an s electron. Since the moment of momentum of an s orbit is zero, the value of L is unchanged by the addition of the s orbit, and hence the type of the terms is the same as with p^3 alone. The value of R is moved up a half or down a half by the addition of the s orbit, and hence the multiplicity is pushed up one or down one. This means that the quartet S of the p^3 configuration is changed to a triplet S and a quintet S, the doublet P to a singlet P and a triplet P, and the doublet D to a singlet D and a triplet D. Only the triplet S, P, and D terms have been observed, and these through their combination with the triplet P of the s^2p^2 configuration, giving rise to the groups at 645 A, 916 A, and 1085 A respectively.

The only other line of N_{II} observed thus far in the study of the extreme ultra-violet which we have been pursuing with our hot-spark technique is the group at 1276 A, which is produced by the change from the configuration $s^2p\,.\,p$ to sp^3. This last is of peculiar interest because it represents the jumping of an electron from $3p$ to $2p$ simultaneously with the elevation of another electron from an s to a p orbit.

This is an unusually interesting form of two-electron jump.

In the discussion of N_{II} we have covered in effect all four-electron systems, such as C_I, N_{II}, O_{III}, and F_{IV}.

5. *Five-electron Systems.*

The typical five-electron system which we shall choose for discussion is O_{II}. The ground state is the s^2p^3 configuration; and since the s^2 has zero momentum, this configuration is precisely the same as the p^3 configuration discussed on p. 575 under the head of a three-electron system. It gives rise to quartet S, doublet P, and doublet D terms.

The first excited state is $s^2p^2.s$, which is identical with the sp^2 configuration discussed on p. 574 under a three-electron system. Its terms are doublet S, doublet D, doublet P, and quartet P. In returning to the ground state the doublet S combines with the doublet P to produce the unresolved pair at 644 A. The jump ^2D to ^2P gives the unresolved group at 601 A. The jump ^2P to ^2P gives the partially resolved group at 673 A. The jump ^2P to ^2D gives the partially resolved group at 617 A. The jump ^4P to ^4S gives rise to the three-line group at 539 A.

The second excited state is $s^2p^2.p$, the terms of which can be obtained by adding to the p^2 terms of a two-electron system (see p. 572) a single p electron. These p^2 terms were ^1S, ^3P, and ^1D, and they change as follows: ^1S changes to ^2P; ^3P changes (since its former values $L=1$, $R=1$ have changed to $L=0$, 1, and 2, and $R=\frac{1}{2}$ and $1\frac{1}{2}$) to ^2S, ^2P, ^2D, ^4S, ^4P, ^4D; and ^1D changes (since $L=2$, $R=0$ changes to $L=1$, 2, 3, $R=\frac{1}{2}$) to ^2P, ^2D, and ^2F. The return from this second excited state to the first excited state produces a large number of lines in the visible which are outside the range of our extreme ultra-violet studies, and have actually been identified in the main by A. Fowler.

The third excited state is $s^2p^2.d$, the terms of which can be obtained as above by adding to the p^2 terms of a two-electron system a single d electron. Then ^1S changes to ^2D; ^3P changes (since its former values $L=1$, $R=1$ have changed to $L=1$, 2, or 3, $R=\frac{1}{2}$ or $1\frac{1}{2}$) to ^2P, ^2D, ^2F, ^4P, ^4D, ^4F; and ^1D changes (since $L=2$, $R=0$ changes to $L=0$, 1, 2, 3, 4 and $R=\frac{1}{2}$) to ^2S, ^2P, ^2D, ^2F, ^2G. The return of this third excited state to the second excited state gives rise to a large number of lines in the visible, also identified mainly by A. Fowler. The return from this third excited state to the ground state, however, produces lines which are in the main

field of our studies. They are as follows:—The ^2P based on the ^3P of the core combines with the ^2D of the ground state to produce the unresolved line at 484 A, and with the ^2P of the ground state to produce the unresolved line at 518 A. The ^2D based on the ^3P of the core combines with the ^2D of the ground state to produce the unresolved line at 481 A, and with the ^2P of the ground state to produce the partially-resolved group at 516 A. The ^2F based on the ^3P of the core combines with the ^2D of the ground state to produce the unresolved line at 485 A. The ^2P based on the ^1D of the core combines with the ^2D of the ground state to give the unresolved line at 440 A. The ^2D based on the ^1D of the core combines with the ^2P of the ground state to give the unresolved line at 470 A, and with the ^2D of the core to give the unresolved line at 442 A. The ^4P based on the ^3P of the core combines with the ^4S of the ground state to give the unresolved line at 430 A.

The fourth excited state which we shall consider is sp^4, *i. e.* one of the two s electrons goes over into one of the p orbits. The simplest way to treat this case is to make use of the general principle that a single vacancy in a shell acts like a single electron in that shell, two vacancies like two electrons, etc., so that since the p can hold but six electrons, p^4 is equivalent to p^2. This means that sp^4 is the same as $p^2 s$, found on p. 574 to possess the terms ^2S, ^2D, ^2P, and ^4P. In returning to the ground state the ^2D going back to ^2P gives rise to the unresolved strong line at 797 A, and in going back to ^2D to the strong partially-resolved line at 719 A. Also the ^2P going back to ^2P produces the partially-resolved group at 581 A, and in going back to ^2D produces the partially-resolved group at 538 A. Again, the ^4P going back to the ^4S produces the very strong three-line group at 834 A.

In the discussion of O_{II} we have covered in effect all five-electron systems such as N_I, O_{II}, F_{III}.

6. *Six-electron Systems.*

The most completely analysed case of a six-electron system is the arc spectrum of oxygen, the greater part of whose lines in the visible have been identified for thirty years. Recently, too, the ultra-violet lines of O_I have been well classified by Hopfield.

The six-electron system which has become partially known through our studies in hot-spark spectrometry is F_{II}. The ground state is s^2p^4, which, by virtue of the principle stated in a preceding paragraph, has terms identical with p^2,

namely ^1S, ^3P, ^1D. The first excited state is $s^2p^3.s$, which has been fully treated under a four-electron system, and has the terms ^5S, ^3S, ^3P, ^1P, ^3D, ^1D. The only group of lines due to it which we have identified is that produced by the combination of ^3S of the first excited state with ^3P of the ground state. This gives rise to the group of three resolved lines at 548 A. The second excited state $s^2p^3.p$ through its return to the first excited state $s^2p^3.s$ should give rise to lines in the visible or near ultra-violet, which, however, have not yet been identified. Also the third excited state $s^2p^3.d$ through its return to $s^2p^3.p$ should also give lines in the visible, but in its return to the ground state s^2p^4 it should give lines in the region of our hot-spark studies. We have, however, not identified with certainty any of this group.

An excited state which actually occurs more frequently than this is the sp^5 configuration, and the drop back from this into the ground state then produces the very strong group of lines at 607 A. The theoretical analysis is here simple, since a p^5 configuration, which corresponds to a vacancy of one in the p shell, is the same as a single p electron configuration. This has a value of $L=1$, $R=\frac{1}{2}$, and when a single s electron is added to this it yields $L=1$, $R=0$ or 1, *i. e.* singlet and triplet P terms. These should combine with the ^1S, ^3P, D of the ground state to produce singlet and triplet lines, of which, however, only the triplets mentioned above are found. These should constitute a group of six lines, which they are actually found to be.

7. *Seven-electron Systems.*

The only possible seven-electron system of this group is F_I, the ground state of which is s^2p^5, which is the same as a single p orbit, *i. e.* it gives rise to a ^2P term. The most probable excited states are, of course, $s^2p^4.s$, $s^2p^4.p$, $s^2p^4.d$, and since the p^4 is equivalent to p^2, these are equivalent to the $s^2p^2.s$, $s^2p^2.p$, $s^2p^2.d$, which were treated above under the five-electron system. The ^2P of the $s^2p^4.s$ combines with the ^2P of the s^2p^5 configuration to produce the four strong lines at 955 A. Also the observed pair of lines at 807 A is due to the return from one of the terms of the $s^2p^4.d$ configuration to the ^2P term of s^2p^5.

References.

1. Fowler, ' Series in Line Spectra,' p. 97.
2. Bowen and Millikan, Phys. Rev. xxviii. p. 256 (1926).
3. Bowen, Phys. Rev. xxix. p. 231 (1927).
4. Bowen and Millikan, Phys. Rev. xxvi. p. 310 (1925).

5. Bowen and Millikan, Proc. Nat. Acad. Sci. x. p. 199 (1924).
6. A. Fowler, Proc. Roy. Soc. cv. p. 299 (1924).
7. Millikan and Bowen, 'Nature,' cxiv. p. 380 (1924).
8. Kiess, J. O. S. A. & R. S. I. xi. p. 1 (1925).
9. Hopfield, Phys. Rev. xxvii. p. 801 (1926).
10. A. Fowler, Proc. Roy. Soc. cvii. p. 31 (1925).
11. Laporte, J. O. S. A. & R. S. I. xiii. p. 13 (1926).
12. Bowen and Millikan, Phys. Rev. xxvi. p. 150 (1925); Bowen and Ingram, Phys. Rev. xxviii. p. 447 (1926).
13. Bowen and Millikan, Phys. Rev. xxiv. p. 212 (1924).
14. A. Fowler, 'Series in Line Spectra,' p. 166.
15. Hopfield, Astrophys. J. lix. p. 114 (1924).
16. A. Fowler, Proc. Roy. Soc. cx. p. 476 (1926).
17. Bowen and Millikan, Phys. Rev. xxvii. p. 144 (1926).
18. De Bruin, *K. Akad. Amsterdam Proc.* xxxv. p. 751 (1926).
19. Paschen, 'Seriengesetze der Linienspektren,' p. 30.
20. Lyman and Saunders, Proc. Nat. Acad. Sci. xii. p. 92 (1926).
21. Bowen and Millikan, Phys. Rev. xxiv. p. 209 (1924).
22. Millikan and Bowen, Phys. Rev. xxiv. pp. 209–228 (1924), and especially Phil. Mag. xlix. p. 923 (1925).
23. Uhlenbeck and Goudsmit, *Naturwissenschaften*. xiii. p. 953 (1925).
24. Russell and Saunders, Astrophys. J. lxi. p. 38 (1925).
25. Pauli, *Zeit. f. Phys.* xxxi. p. 765 (1925).
26. Heisenberg, *Zeit. f. Phys.* xxxii. p. 841 (1925).
27. Hund, *Zeit. f. Phys.* xxxiii. p. 345 (1925).
28. Millikan, Proc. Nat. Acad. Sci. vii. p. 289 (1921).
29. Payne, 'Stellar Atmospheres,' p. 15 (1925).

LI. *Structure of the Radioactive Atom and Origin of the α-Rays.* *By* Sir Ernest Rutherford, *O.M., P.R.S., Cavendish Professor of Experimental Physics, University of Cambridge* *.

§1. In the course of the last twenty years, a large amount of accurate data has been accumulated on the emission of energy from radioactive atoms in the form of α, β, and γ rays, and in the majority of cases the average life of the individual elements has been determined. This wealth of data on atomic nuclei, which must have an intimate bearing on the structure of these radioactive atoms, has so far not been utilized as our theories of nuclear structure are embryonic. We are not yet able to do more than guess at the structure even of the lighter and presumably least complex atoms, and for this reason it would appear at first sight that we could not hope to attack, with any chance of success, the problem of the structure of the radioactive nucleus which must contain many more individual units in its constitution than the lighter atoms. However, it has

* Communicated by the Author.

always seemed to me possible that the structure of the heavy nucleus might present certain simple general features which may be either absent or difficult to detect in the lighter atoms. Moreover, in the case of the heavy radioactive atoms we have a great variety of quantitative data with which to test the validity of any working theory.

The simple theory of the origin of the α-rays which I shall outline in this paper had its inception in the endeavour to reconcile apparently conflicting results on the dimensions of the nucleus obtained by different methods. The experiments on the scattering of α-particles have shown that the Coulomb law of force is widely departed from in close collisions of swift α-particles with light atoms, but no deviation has so far been observed for the heavy atoms of high nuclear charge. For example, the scattering by silver and gold of the swiftest α-particles available is in close accord with an inverse square law of electric force, and although the data on uranium, on account of the difficulty of obtaining thin uniform films, are not so definite, yet we could not find any certain indication of the failure of the inverse square law for this element, although the α-particle must have approached within $3{\cdot}2 \times 10^{-12}$ cm. from the centre of the uranium nucleus. Since we should anticipate that the law of the inverse square must break down when the α-particle enters the charged region of the nucleus, these experiments appear to indicate that the nucleus of uranium must have a radius less than $3{\cdot}2 \times 10^{-12}$ cm. On the other hand, the radioactive data strongly suggest that the nuclear structure must extend to a distance of at least 6×10^{-12} cm. This deduction is based on the following argument. When an α-particle carrying two positive charges is released from the nucleus, it must gain energy in escaping through the repulsive electric field due to the nucleus. The energy gained by the α-particle in passing from a distance r from the nucleus is $2Ze^2/r$, where Ze is the nuclear charge of the residual atom. Even if the α-particle escapes with no initial velocity, its energy cannot be less than this amount. Now the slowest α-particle, which is emitted by Uranium I, has an energy corresponding to $4{\cdot}07 \times 10^6$ electron-volts. Taking the charge on the nucleus after release of the α-particle as $90e$, it follows that the value of r cannot be less than $6{\cdot}3 \times 10^{-12}$ cm. and must be greater if the α-particle has any initial velocity. In other words, the dimension of the nucleus computed from radioactive data is at least twice as great as that indicated by a study of the scattering of α-particles.

It does not seem possible to explain away this divergence by assuming that the α-particle leaves the nucleus carrying only one charge, for the change in the atomic number of the element by expulsion of an α-particle shows that it always carries two charges away from the nucleus. On the radioactive data, it seems clear that, if the outer nucleus contains an excess of positive charge, the scattering experiments ought to show a departure from a Coulomb law of force for even slow α-particles. The failure to detect any change in the law of force indicates that either the component parts of the outer nucleus are uncharged or that there is on the average a uniform distribution of positive and negative charges.

The electrical forces from the nucleus on a positively charged body are repulsive and the experimental evidence on the scattering of α-particles by aluminium and magnesium indicates that the attractive forces which come into play due to the distortion or polarization of the main nuclear structure by the charged α-particle only become of importance at distances of about 1×10^{-12} cm. We are thus led to the conclusion that if any constituent particles of the nucleus extend to 6×10^{-12} cm., they must be electrically neutral. If we suppose that neutral particles are in circulation round the central nucleus, they can only be held in equilibrium by attractive forces due to the *distortion* or *polarization* of the particle itself by the electric field or to magnetic forces arising from the central nucleus *. No definite information is available as to the magnetic state of the nucleus, so in the present theory we shall confine ourselves to forces of attraction due to the polarization of the structure of the neutral satellite by the electric forces arising from the main nucleus. It will be seen that this will give rise to attractive forces of the right order of magnitude to retain a satellite in a quantum orbit round the nucleus.

One of the most striking facts in radioactive transformations is the constancy of the speed with which an α-particle is expelled from a given radioactive atom. The recent experiments of Irene Curie on the α-rays from polonium and of G. Briggs on the α-rays from radium C show that the speeds of the issuing rays are identical for each element within the limits of measurements, viz., about 1 in 1000.

* Debye, and in more detail Hardmeier, have calculated the change in scattering of the α-particle by aluminium and magnesium on the assumption that an attractive force varying as $1/r^5$ arises due to the polarization of the nucleus by the α-particle. In the present satellite theory, we are dealing with the different case of the distortion of the neutral satellite due to the field from the nucleus.

This uniformity of speed is a strong indication that the α-particle in the nucleus is circulating in a quantized orbit and is released at a definite characteristic velocity.

§ 2. Suppose a neutral satellite of mass m is moving in a circular orbit of radius r with a velocity v under the influence of an attractive force due to polarization of its structure by the electric field due to a central nucleus of charge Ze.

The attractive forces F on an insulated conducting sphere of radius a due to a point charge Ze at a distance r is given by

$$F = \frac{Z^2e^2(2r^2-a^2)}{r^3\ (r^2-a^2)^2}$$

$$= \frac{2Z^2e^2a^3}{r^5}\left(1+\frac{3}{2}\frac{a^2}{r^2}+\ldots\right) \quad . \quad . \quad . \quad . \quad (1)$$

if a/r is small.

Neglecting for a moment the correction term, the equilibrium of the satellite in a circular n quantum orbit is given by

$$mvr = nh,$$

$$mv^2/r = 2Z^2e^2a^3/r^5, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where h for simplicity is used as a symbol for $2\pi\times$ (Planck's constant).

From these equations

$$r = \surd 2\,Zea^{3/2}m^{\frac{1}{2}}/nh \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and $$\tfrac{1}{2}mv^2 = n^4h^4/4a^3m^2Z^2e^2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

is the kinetic energy of the particle in its orbit.

It will be seen that $r \propto 1/n$, so that the higher the quantum number the smaller the radius of the orbit and the swifter the motion of the particle. The loss of energy w_1, due to the removal of the satellite from a distance r to an infinite distance against the attractive forces of polarization, is given by

$$w_1 = 2Z^2e^2a^3\int_r^\infty dr/r^5 = Z^2e^2a^3/2r^4 \quad . \quad . \quad . \quad . \quad (5)$$

From equation (2), it is seen that this is one half of the kinetic energy of the particle in its orbit, so that, if the particle for any cause is released from its orbit, it should escape with one half of its original energy of motion. It is clear also that on ordinary mechanics the quantum orbit is unstable since if it is disturbed the particle should escape

from its orbit, but we do not yet know how to interpret instability in quantum mechanics.

For orbits closer to the nucleus, the value of a/r in (1) may become comparable with unity. Making this first order correction, it is easily shown that the energy of the satellite in its orbit is to a first approximation given by

$$\tfrac{1}{2}mv^2=\frac{n^4h^4}{4a^3m^2Z^2e^2}\left(1-\frac{3}{4}\frac{n^2h^2}{amZ^2e^2}\right). \quad . \quad . \quad . \quad (6)$$

The loss of energy w_1 of the particle escaping against the attractive forces is given in this case by

$$w_1=\frac{a^3Z^2e^2}{2r^4}\left(1+\frac{a^2}{r^2}\right). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The energy E of motion of the particle after its escape can be shown to be

$$\mathrm{E}=\tfrac{1}{2}mv^2-w_1=\frac{n^4h^4}{8a^3m^2Z^2e^2}(1-bn^2), \quad . \quad . \quad (8)$$

where $b=h^2/maZ^2e^2$.

§ 3. *Application to the α-particle.*

We have so far dealt with the case of any neutral satellite which remains uncharged during its escape from the atom. We shall next consider the modifications in the theory in order to account for the velocity of escape of the α-particles from a radioactive atom. For the reasons already given, we shall suppose that the α satellites are electrically neutral circulating in quantum orbits under the attractive forces due to polarization of their structure by the field from the central nuclear charge. Such a neutral α-particle must consist of a helium nucleus which has gained two electrons. These electrons cannot occupy the same positions as in the ordinary helium atom in the free state, for they would then not be part of the main nucleus at all. They must be bound much more closely to the helium nucleus, probably circulating in orbits which are rendered possible only by the distortion of the nuclear structure of the α-particle by the intense electric or magnetic fields due to the central nucleus. In fields below a critical value, the electron orbits may not be possible and consequently a neutral α-particle in escaping from the nuclear structure would be robbed of its two electrons when the field falls to the critical value. It is an essential part of the present

theory that the satellite must lose its two electrons before its complete escape from the nucleus. Such a passage from a neutral to a charged particle is essential in order to fulfil the well established observation that the nuclear charge of an atom is lowered by two units when an α-particle is expelled. It follows also that the electrons liberated from the satellite during its escape must fall back towards the nucleus and be incorporated in its structure *.

It is difficult to estimate the binding forces which hold the electrons in equilibrium in the satellite. They must be strongly bound in order to be retained in the intense nuclear field and probably circulate in the region close to the helium nucleus where we know from scattering experiments the forces are abnormal and much greater than is to be expected on a Coulomb law of force. It may be that the electron orbits become automatically unstable when the distorting forces acting on the satellite fall below a certain value and are released from the satellite. The energy for disruption may be in part acquired from the energy stored in the distorted nucleus, and in part from the energy of motion of the satellite.

If the satellite loses its two electrons at a distance r from an atom of initial charge Ze, the energy acquired in passing through the repulsive field is $2(Z-2)e^2/r$. Consequently if the satellite for some reason is released with its velocity in the orbit of quantum number n, the final energy E of release of the α-particle from the atom of number Z is given approximately by

$$E=2(Z-2)e^2/r-w_2+\frac{n^4h^4}{8a^3m^2Z^2e^2}(1-bn^2), \quad . \quad (9)$$

where w_2 is the kinetic energy lost by the satellite in the process of the removal of the two electrons. The approximations are specified below.

For atoms of the same number Z, the value

$$E=A+Bn^4(1-bn^2), \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where A and B are constants, A including the first two terms. In practice, it is convenient for calculation to fix the values of A and B for a standard atomic number by comparison with the experimental data. The number chosen is 84, which includes at least seven groups of α-particles. The

* Frl. Meitner suggested some time ago that *some* of the α-particles existed in the neutral state within the nucleus in order to account fo the observation that in several cases, two β-ray changes follow an α-ray change.

values for atoms of different charge are then deduced by a percentage correction of each constant for Z in equation 9.

The value of r in the first term of equation (9) is dependent to some extent on the atomic number Z. The correction may be estimated in several ways, giving slightly different results.

It is probably best to suppose that the neutral particle loses its electrons when the energy stored in the satellite due to distortion falls below a certain critical value, the same for all α-particles. The expression for this quantity is given in equation (7), where r is taken as the distance from the central nucleus for disruption. Neglecting the term a^2/r^2, it is seen that $r \propto \sqrt{Z}$, so that the value of the first term in (9) varies as $(Z-2)/\sqrt{Z}$ or to a near approximation $\sqrt{Z}$.

In the absence of any definite information as to the value of w_2 included in the constant A, we shall apply the correction for atomic number to A as a whole, although this probably somewhat underestimates the true value of the correction. The value of b is seen from (8) to vary as $1/Z^2$.

If Z_0 is the number * of the element used as a standard, the value of E for an element of number Z is given by

$$E = A\sqrt{Z/Z_0} + \frac{BZ_0^2}{Z^2} n^4 \left(1 - \frac{Z_0^2}{Z^2} bn^2\right). \quad . \quad . \quad (11)$$

It should be mentioned that in these calculations the retarding forces on the satellite during its escape are integrated from r to ∞ (eq. 7), while in the application to the α-particle, the latter is supposed to lose its electrons at a definite distance from the nucleus when the field falls to a certain value. No information is available as to the relative forces due to polarization in the charged and neutral satellite, but it will be seen that the change in the calculated energy due to this would in practice be included in the constant A, deduced by comparison of the theory with the experimental data.

§ 4. *Comparison with experiment.*

In order to compare theory with experiment, it is necessary to fix the values of the constants A, B, and b and the value of n by consideration of the energy of the different groups of emitted α-particles. As a result of a large amount of trial calculation, the values of these constants were adjusted

* Since the satellites are electrically neutral, the charge on the central nucleus is given numerically by the atomic number.

to make the best fit with the known energy of the eight groups of α-particles emitted during the uranium-radium series of transformations. Since the energy of the emitted α-particles is dependent only on the nuclear charge of the element and the quantum number of the orbit, the α particles from the thorium and actinium series should fit the same equation with exactly the same value for the constants A, B, and *b*. Consequently, the theory, if correct, should give the energy of emission of the α-particles from all radioactive elements in terms of only one variable connected with the quantum number *n*.

In 1921, Geiger * measured with great care the ranges of the α-particles emitted from all the radioactive elements with the exception of Uranium I, Uranium II, and Thorium. He had long before shown that the velocity V of the α-particle is connected with its range R by the equation $V^3 = KR$. Recently G. Briggs † has shown that this relation holds fairly closely for α-particles of range between 7 cm. and 3 cm., *i. e.* over a range covering practically all the known groups of α-particles.

The results obtained by Geiger are given in Table I. The ranges of the groups of α-particles in air are given for 15° C. and 760 mm. pressure. The probable error in the determination estimated by Geiger is given in column 3. The velocity and energy of the α-particles are determined by the relation $V^3 = KR$, from the known velocity of the α-particles of radium C which have an extrapolated range 6·971 cm. This velocity is known from the experiments of Rutherford and Robinson to be $1{\cdot}922 \times 10^9$ cm./sec.

The energy of emission of the α-particle is most conveniently expressed in electron-volts, *i. e.* in terms of the potential difference required to give an electron the energy of the α-particle. The energy of the α-particle from radium C, which is taken as a standard of comparison, is 7·662 million volts.

The ranges given for the α-particles from Ur. I and Ur. II are those recently found by Lawrence ‡ by measuring the lengths of the α-ray tracks in a Wilson expansion chamber. They are believed to be correct to within about one per cent. and differ somewhat from the original determination of Geiger and Nuttall §, viz. 2·67 and 3·07 cm. respectively. Before I knew of the results of Lawrence,

* *Zeit. f. Phys.* viii. p. 45 (1921).
† Proc. Roy. Soc. A, 114. pp. 313, 341 (1927).
‡ Trans. Nova Scotia Inst. 1927.
§ Phil. Mag. xxiii. p. 439 (1912).

I had satisfied myself by the scintillation method that the range of the α-particles from Ur. II was greater than that given by Geiger and not less than 3·23 cm.

The data for protoactinium and thorium itself are only approximate.

TABLE I.

Element.	Range in cm. in air at 15° C. and 760 mm.	Mean error in cm.	Velocity in cm./sec. $\times 10^9$.	Energy in volts $\times 10^6$.
Uranium I	2·70	...	1·406	4·07
Uranium II	3·28	...	1·495	4·64
Ionium	3·194	$\pm$0·016	1·482	4·554
Radium	3·389	„ 0·009	1·511	4·735
Radon	4·122	„ 0·009	1·613	5·397
Radium A	4·722	„ 0·010	1·688	5·908
Radium C	6·971	„ 0·004	1·922	7·662
Radium F	3·925	„ 0 004	1·587	5·223
Protoactinium ...	3·673	„ 0·042	1·552	4·998
Radioactinium ...	4·676	„ 0·025	1·683	5·871
Actinium X	4·369	„ 0·019	1·645	5·610
Actinon	5·789	„ 0·017	1·807	6·769
Actinium A.....	6·584	„ 0·010	1·886	7·373
Actinium C.....	5·511	„ 0·006	1·777	6·551
Thorium	2·90	uncertain	1·435	4·27
Radiothorium.....	4·019	$\pm$0·005	1·600	5·306
Thorium X.....	4·354	„ 0·010	1·643	5·598
Thoron	5·063	„ 0·007	1·728	6·291
Thorium A.....	5·683	„ 0·008	1·796	6·685
Thorium C.....	4·787	„ 0·009	1·696	5·963
Thorium C'.....	8·617	„ 0·007	2·063	8·825

The agreement between theory and experiment is shown in Table II. In column 3 is given the quantum number n selected by trial; column 4 the value of $n_1 = n + \frac{1}{2}$ which will be used in calculating the energy of the α-particle (eq. 11); column 5 the calculated value of $Bn_1^4(1 - bn_1^2)$ for atomic number 84; column 6 the same quantity corrected for atomic number; column 7 the value of A corrected for atomic number; column 8 the calculated energy by adding columns 6 and 7; column 9 the observed energy given in Table I.

The value of the constants used in these calculations are for atomic number 84:

$$A = 3{\cdot}600 \times 10^6 \text{ electron-volts.}$$
$$B = 6{\cdot}856.$$
$$b = 1{\cdot}25 \times 10^{-4}.$$

TABLE II.

1	2	3	4	5	6	7	8	9	
Element.	Atomic number.	Quantum number n.	Quantum number $n_1 = n + \frac{1}{2}$.	$Bn_1^4(1-bn_1^2)$ for at. no. 84 in millions of volts.	$Bn_1^4(1-bn_1^2)$ corrected for at. no. in millions of volts.	A corrected for at. no. in millions of volts.	Calculated energy of α-particle in millions of volts.	Observed energy of α-particle in millions of volts.	% Difference, Col. 8 & 9.
Uranium I	92	14	14·5	·295	·245	3·77	4·015	4·07	1·4
,, ,, ...	,,	14·5	15	·337	·280	,,	4·05	,,	0·5
Uranium II	92	19·5	20	1·042	·873	3·77	4·64	4·61	0·0
Ionium	90	19	19·5	·944	·825	3·729	4·554	4·554	0·0
Radium	88	20	20·5	1·146	1·047	3·687	4·734	4·737	0·1
Radon	86	22·5	23	1·793	1·714	3·643	5·357	5·396	0·8
Radium A..... ..	84	24	24·5	2·283	2·283	3·600	5·883	5·910	0·5
Radium C.....	84	28	28·5	4·062	4·062	3·600	7·662	7·662	0·0
Radium F (Po)...	84	22	22·5	1·644	1·644	3·600	5·244	5·224	0·4
Thorium	90	17	17·5	·618	·539	3·729	4·27	4·27	0·0
Radiothorium ...	90	22·5	23	1·793	1·569	3·729	5·298	5·306	0·2
Thorium X	88	23·5	24	2·111	1·931	3·687	5·618	5·598	0·4
Theron	86	25	25·5	2·664	2·549	3·643	6·192	6·191	0·0
Thorium A	84	26	26·5	3·082	3·082	3·600	6·682	6·685	0·0
Thorium C	83	24	24·5	2·283	2·335	3·578	5·913	5·963	0·9
Thorium C′	84	30	30·5	5·239	5·239	3·600	8·839	8·825	0·2
Protoactinium ...	91	21·5	22	1·510	1·291	3·750	5·041	4·998	0·8
Radioactinium ...	90	24·5	25	2·471	2·168	3·729	5·897	5·871	0·5
Actinium X	88	23·5	24	2·111	1·931	3·687	5·618	5·610	0·0
Actinon	86	26·5	27	3·313	3·171	3·643	6·814	6·769	0·6
Actinium A	84	27·5	28	3·801	3·801	3·600	7·401	7·373	0·4
Actinium C	83	25·5	26	2·867	2·933	3·578	6·511	6·551	0·6

The reasons for the choice of the particular form of n and its magnitude will be discussed in the next section. It suffices to say here that n may vary by half quantum numbers, *e.g.* 24, 24·50, 25, and $n_1 = n + \frac{1}{2}$ nearly. It will be seen later that the value of n deduced from the experimental data on the α-rays is in excellent accord with the theory and our general knowledge of the dimensions of nuclei.

On the whole there is a very fair agreement between theory and experiment. The calculated values of the energy of emission of at least seven groups of α-particles agree within a small fraction of a per cent. with the observed values, while in a number of other cases the agreement is within the probable experimental error. Although the values of the constants in the equation were chosen to give the best fit with the α-particles from the uranium-radium series, it will be observed that with one exception the agreement for the thorium series is even better.

It might at first sight be thought that a fair agreement between theory and experiment is to be anticipated when n_1 has such a large value and may vary by half units. It must be remembered, however, that the energy-term due to the motion of the satellite varies as the fourth power of the quantum number, and calculation shows that it is very unlikely that the many close coincidences are fortuitous. For example, consider the change in energy of the emission of α-particles from an element of atomic number 84, corresponding to the successive quantum numbers $n_1 = 26$, 26·5, 27. The calculated energies of emission are 6·467, 6·682, 6·913 million volts varying about 3 per cent. from one number to the next. The observed value for the α-particles from thorium A is 6·685 million volts differing very slightly from the calculated value for $n_1 = 26{\cdot}5$. The case is different for α-particles of low energy, *e.g.* those emitted from Uranium I. and II., where the value of the constant A represents a large part of the total energy. In such cases the quantum number cannot be fixed with the same certainty unless the energy of emission of the α-particles is known with great accuracy.

At this stage it is of little value to discuss in any detail the agreement between theory and experiment. Unfortunately, there still remains some uncertainty as to the correct values of the energies of emission of the groups of α-particles. The velocities of the α-particles have not been determined directly but deduced from measurements of the range of the α-particles in air, and an appreciable error may arise due to

this cause. In some cases, when there is a mixture of α-ray products, it is difficult to be certain of the accuracy of the ranges, however much care is taken in making the observations.

It is important to develop new direct methods of measuring the velocity of emission of the α-particles with the greatest possible precision. If the relative energies of the main groups of α-particles could be determined with certainty to 1/500 or still better to 1/1000, it would then be possible to test the theory in detail.

It should, however, be pointed out that for several elements, notably radon, thorium C, and actinium C, the calculated and observed values differ by considerably more than the experimental error estimated by Geiger. It is not possible to reduce the disagreement notably by adjustment of the constants. It seems clear that if the experimental results are reliable there is a real discrepancy between the theory and experiment.

There is, however, one factor which has been neglected in this calculation. It has been assumed that the forces in the neutral satellite are entirely due to its polarization by the electric field, and no account has been taken of the effect of magnetic forces acting on the satellite. Unfortunately, we have no knowledge of the magnetic state of the satellite or of the radioactive nuclei. Even if the α satellite has no permanent magnetic moment, it is quite possible that the central nuclei may have a magnetic moment which may vary from one nucleus to the next. If we suppose that the nucleus has a magnetic moment, it will exert an attractive force due to the magnetic polarization of the satellite, even if the latter has no permanent magnetic moment itself. No doubt the attractive force due to this cause will vary more rapidly with the distance than the attractive force due to the electric field. If this force is small compared with that due to the electric polarization, the effect of the addition of a magnetic attraction would be analogous to an increase in the nuclear charge. A decrease of the magnetic moment of the nucleus would correspond to the effect of a diminution of the nuclear charge. The marked discrepancy in certain cases between calculation and experiment, if not due to experimental error, may thus possibly be ascribed to a difference in the magnetic moment of the nuclei. At this stage no data are available to estimate the magnitude of this effect, but it may quite likely prove of importance and may have to be taken into account in any complete theory. It would be of great interest if methods could be

found for determining the magnetic moment of radioactive nuclei *.

In this connexion, it is of interest to note that, in the case of the actinium family, the theory in most cases gives a somewhat higher energy for the α-particles than the observed values. This discrepancy would be largely removed if it be supposed that the value of B in equation 11 is about one per cent. less for the nuclei in the actinium group than for the nuclei in the thorium and Ur-Ra group. This would correspond to the effect of an increase of the nuclear charge of about one half per cent., and on the views outlined above would indicate that, with the exception possibly of actinium C, the nuclei of the actinium group have on the average a higher magnetic moment than that for the other two radioactive series. However, any conclusions on these points should be reserved until we are certain of the accuracy of the experimental data.

§ 5. *Quantum number of satellites and dimensions of orbits.*

In the new or wave mechanics the value of n, where n is the quantum number of an angular momentum on the old calculations, is always replaced by $(n+1)$ or $n(n+\frac{1}{2})^2$ nearly when n is large †. We should consequently expect the value n^4 in the expression for the energy of motion of the satellite to be replaced by $(n+\frac{1}{2})^4$. It is for this reason we tabulate n_1 in column 4, Table II.

We must now consider the dimensions of the quantum orbits supposed circular. For simplicity of calculation, we shall suppose that the forces on the satellite vary as $1/r^5$ and thus neglect the correction term. Since under these conditions the satellite loses half its orbital kinetic energy in escaping against the attractive forces, the orbital energy of the satellite expelled from radium C, $n=28$, is equal to 8·12 million electron-volts. This corresponds to an orbital velocity $1{\cdot}98\times10^9$ cm./sec., which is slightly greater than the ultimate velocity of escape of the α-particle from the nucleus. Substituting the value of V in equation $mvr=nh$ and taking $n=28$ and $m=$the mass of the helium atom $=6{\cdot}60\times10^{-24}$,

$$r=2{\cdot}24\times10^{-12} \text{ cm. for an atomic number 84.}$$

* S. Goudsmid and E. Back (*Zeit. f. Phys.* xliii. p. 321, 1927) suggest that the superfine structure in the bismuth optical spectrum may be due to the magnetic moment of the bismuth nucleus. This mechanical moment from which this arises is estimated to be about $9h/2$.

† *Vide* O. W. Richardson, "Present State of Atomic Physics," Proc. Phys. Soc. (1927).

Since $r \propto Z/n$, the value of r for the outermost orbit of Ur I., number 14, is $4{\cdot}09 \times 10^{-12}$ cm.

For such an orbit to be possible, this distance must be smaller than the critical distance at which the satellite loses its electrons. Since the value of the constant A, viz. 3·77 million volts for atomic number 92, represents mainly the energy gained by the charged α-particle in escaping through the repulsive field, it can readily be calculated that the critical distance from this nucleus must be less than $r = 6{\cdot}8 \times 10^{-12}$ cm., corresponding to a quantum number about 8 to 10.

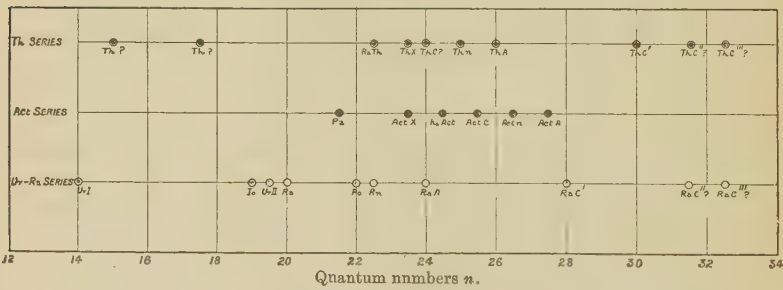
The distances involved are thus in accord with the theory and are of about the magnitude to be expected. There is, however, one difficulty since in some cases, and particularly in the actinium series, half quantum numbers appear. Such half quantum numbers are essential to include all the groups of α-particles of different energies. These half quantum numbers would, of course, disappear if all the quantum numbers are doubled throughout. This, however, is impossible when we take into account the critical distance at which the satellite breaks up. For example, if n is taken as 56 corresponding to the α-particle from radium C, the orbital radius is $4{\cdot}48 \times 10^{-12}$ cm., while the outermost uranium orbit $n = 28$ has a radius $9{\cdot}8 \times 10^{-12}$ cm. This is well outside the critical radius for the satellite, and consequently no such orbit is possible. We may, of course, get over the difficulty by the drastic assumption that the unit of angular momentum is $\frac{1}{2}h$ instead of h, but, apart from this, it seems simplest to suppose that for some reason half quantum numbers are possible, representing subsidiary quantum orbits. We must await a solution of this problem based on the new mechanics to know whether such subsidiary quantum orbits can exist theoretically. We have so far only considered circular orbits, but other more complicated quantum orbits may be possible.

We have made all the calculations on the simple assumption that the quantum numbers are exactly one-half. If, however, we consider the data given in Table II., it will be seen that in the majority of cases, and particularly for the actinium series, the energies calculated on half quantum numbers are on the whole somewhat greater than those observed. If we ascribe the difference entirely to the wrong choice of quantum number, it is easy to estimate that the average quantum number is about $n + {\cdot}52$ instead of $n + {\cdot}50$, chosen for calculation. It is probable, however, as already pointed out, that this discrepancy may be accounted for on quite

different grounds. There is some general evidence that the half quantum orbits exhibit some peculiarities not shown by the whole quantum orbits. In § 8 it will be seen that a simple empirical relation exists between the constant of transformation of a nucleus and the quantum number of the satellite which is liberated, both for the thorium and uranium-radium series. There is evidence of a similar general relation for the actinium series, where the orbits are all characterized by half quantum numbers, but the points of the curve are erratic, and the elements actinium X and actinium C do not fit in at all. In addition, radon, which is characterized by a half quantum orbit, is displaced from the main curve for the Ur-Ra series. (See fig. 2.) It may be that on the average these subsidiary orbits are more complex than the normal orbits and do not show in all cases the same simple relations.

The distribution of quantum orbits, which are known from the expulsion of α-particles, is shown graphically in fig. 1 for the three radioactive series of elements.

Fig. 1.



It will be observed that, considering the three series together, all possible orbits, seven in number, are represented between $n=23{\cdot}5$ and $n=26{\cdot}5$ inclusive. Between $n=19$ and $n=28$ inclusive, representing 18 possible orbits, only 3 are unrepresented, viz., numbers 20·5, 23, 27. It is noteworthy that not only are the quantum numbers deduced in the actinium series all half, but they are less distributed than for the other two series.

It will be noted also that certain quantum orbits are common to two series of elements, viz., 22 ascribed both to polonium and to radiothorium, 24 to radium A and thorium C, and 23·5 to thorium X and actinium X. If we take into account the long range particles from radium C and

thorium C, probably $n=31$ and $n=32{\cdot}5$ are common to the radium and thorium series (see § 7).

It is of interest to consider whether other satellites exist in uranium, thorium, and actinium, in addition to those which are liberated in the series of transformations. There is no definite evidence on this important point, but I think it quite possible that a number of other satellites characterized by definite quantum orbits are present in the three elements. If the evidence discussed in § 9 on the connexion between the α- and γ-rays has any validity, it definitely indicates that a number of the satellites are present which in some cases are transferred from one orbit to another without, however, escaping from the nucleus. The evidence so far available, however, does not fix any definite limit to the number of neutral satellites, possibly in some cases of different masses, which may be circulating in quantum orbits round the central nucleus.

§ 6. *Dimensions of the satellites.*

For the purposes of calculation it has been assumed that the satellite is represented by a conducting insulated sphere of radius a, and the attractive forces have been deduced on this basis. It is important to estimate the magnitude of this radius and to see whether it is consistent with our knowledge of the dimensions of the nucleus. The value of a can be deduced most simply from the constant bn^2 (Equ. 8, 9), which is equal to a^2/r^2 when r is the distance of the satellite from the nucleus. Now we have deduced from the experimental data that $a^2/r^2=bn^2=\cdot1015$ for atomic number 84, where r is the radius of the quantum orbit $n=28$, corresponding to the α-particle from radium C. Since $r=2{\cdot}24\times10^{-12}$ cm. in this case, $a=7{\cdot}0\times10^{-13}$ cm. We can also deduce the value of a by substituting the values corresponding to the α-particle from radium C in equation 2. This gives $a=6\times10^{-13}$ cm. The two numbers are in fair accord and indicate that the equivalent volume of the satellite assumed spherical is about 1×10^{-36} c. cm.

Now the region surrounding the α-particle where the forces are abnormal has been deduced by Chadwick and Bieler to be spheroidal in shape of semi-axes 8×10^{-13} and 4×10^{-13} cm. The volume of this region, $0{\cdot}5\times10^{-36}$ c.cm., is of the same order as the polarization volume of the satellite deduced from the theory. This agreement is satisfactory, for the general evidence indicates that the neutralizing electrons in the satellite must be closely bound to the nucleus, probably circulating close to the region where the forces due to the α-particle become abnormal.

§ 7. *Long range particles.*

We have so far confined our attention to the well-known groups of α-particles emitted from the radioactive series. In addition to these main groups, however, it is now known that a relatively very small number of α-particles of definite range are emitted during the disintegration of the active deposits of radium, thorium, and actinium. These are usually ascribed to the "C" bodies, but their exact origin is unknown. It has been found that radium C emits a few particles of range about 9·3 cm. and a still smaller number of range 11·3 cm. Thorium C emits also two groups, one of range about 9·4 cm. and the other of 11·3 cm. In addition, actinium C emits some particles of range about 6·5 cm. As these particles exist in relatively very small numbers—varying from about 1 in 10^4 to 1 in 10^5 of the main groups—it has been difficult to determine their ranges with accuracy, but it seems clear that they are in all cases helium nuclei ejected at high speed.

We may suppose that while the majority of the atoms break up in one way due to the liberation of the satellite from a definite quantum orbit, a small number of the atoms may liberate satellites from other and presumably more deep-seated orbits.

On the theory outlined, each group of α-particles should correspond to a definite quantum orbit and, if the nuclear charge of the disintegrating atom is known, the energy of the issuing α-particles can be calculated in terms of the quantum number. Assuming that the long range α-particles from radium C and thorium C come from an 84 nucleus, the energy and range of the α-particles corresponding to each quantum number are given in the table below.

Quantum number n.	$n+\frac{1}{2}$.	Energy in millions of volts.	Range in cm. at 15° C., 760 mm.
28	28·5	7·662	6·971 (Rad. C′)
28·5	29	7·941	7·36
29	29·5	8·225	7·75
29·5	30	8·530	8·19
30	30·5	8·839	8·617 (Th. C)
30·5	31	9·175	9·14
31	31·5	9·510	9·64
31·5	32	9·868	10·20
32	32·5	10·236	10·76
32·5	33	10·626	11·39
33	33·5	11·020	12·03

The ranges are calculated from the relation $v^3 = \mathrm{KR}$ in a

region where the accuracy of this relation has not been tested. The calculated ranges are probably somewhat less than the true ranges for such high-speed particles. Experiments are in progress in this laboratory to determine the ranges of these swift particles with more accuracy and to test whether they can be included in one or more of the groups predicted by the theory.

It is not unlikely that the long range particles from radium C′ and thorium C′, the ranges of which have been estimated by the scintillation method to be about 9·3 and 9·5 cm. respectively, may prove to be identical in energy corresponding to a quantum orbit $n=31$ in the two elements. The 11·3 particles from the same elements may in a similar way arise from the same quantum orbit $n=32{\cdot}5$.

With regard to actinium, Bates and Rogers found by the scintillation method that the long range particles from actinium C have a range of 6·49 cm. while the main group has a range 5·511 cm. (Geiger). The range 6·49 cm. corresponds to an energy of the α-particle of 7·30 million volts and may prove to be coincident with the α-particles of actinium A of range 6·584 cm. (Geiger).

§ 8. *Connexion between the radioactive constant and the quantum number.*

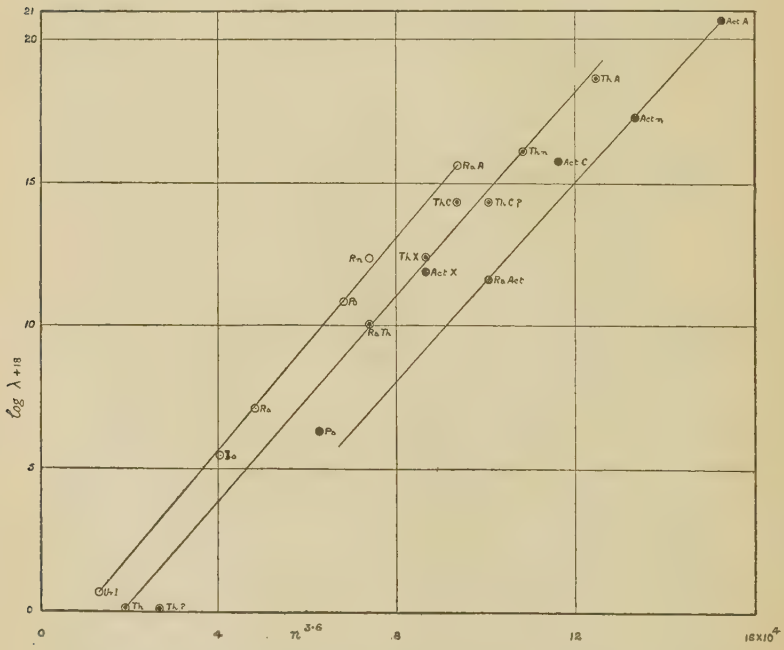
It was long ago shown by Geiger and Nuttall * that the velocity or range of the α-particle in a particular radioactive series increased with the constant of transformation of the element ejecting the α-particle. If the logarithm of the ranges or energies of the α-particles for each radioactive series is plotted against the logarithm of the transformation constant λ, the points lie approximately on a straight line which has a different slope for each radioactive series. This relation has proved very useful in estimating roughly the periods of transformation of elements which cannot be directly determined. When the ranges of the α-particles were redetermined with much more accuracy by Geiger (*loc. cit.*) in 1921, it was found that this rule was only approximate and that there were marked discrepancies, particularly in the actinium series of elements. Lindemann suggested a possible interpretation of the relation observed.

The fact that the energy of the issuing particle must be in part due to the gain of energy in escaping through the repulsive field, makes it doubtful whether the empirical relation found by Geiger has any exact fundamental significance. On the views advanced in this paper, it is to be

* Phil. Mag. xxiii. p. 439 (1912).

anticipated that the radioactive constant λ should be connected not with the final energy of escape of the α-particle, but with the quantum number n characterizing the orbit of the satellite which is liberated, and also, no doubt, with a quantity depending on the constitution of the central nucleus. I find by trial that the radioactive constant λ for each of the elements in one radioactive series can be expressed approximately by a relation of the form $\lambda = ce^{\alpha n^{3\cdot6}}$ or $\log \lambda = c + \alpha n^{3\cdot6}$, where n is the quantum number of the orbit and c and α are factors which are constant for a particular radioactive series but vary from one series to another. The agreement shown by this relation is illustrated in fig. 2,

Fig. 2.



where the ordinates represent $\log_{10}\lambda + 18$ and the abscissæ are proportional to $n^{3\cdot6}$. For both the uranium and thorium series, the elements, with the exception of radon and thorium C, lie nearly in a straight line. This simple relation is much less obvious for the actinium series, for actinium X and actinium C are much displaced from the straight line drawn through the other products. This peculiarity of actinium has been referred to in § 5, where it is suggested

that this may be connected with the fact that the α-particles from the actinium series are characterized by half or subsidiary quantum numbers. It may be that the difference in the constants c and α for the three series, which presumably depend on the detailed structure of the central nucleus, are in some way connected with differences in the magnetic state of the central nucleus.

It should be pointed out that the line for the Ur-Ra series fits best with the assumption that the α-particle from Ur I is connected with a quantum number 14 rather than 14·5, which happens to fit in a little better with the existing data (Table II). In the case of thorium, the trend of the curve indicates that the α-particle from thorium itself depends on $n=14{\cdot}5$ or 15 rather than $n=17$, which happens to agree with the very uncertain data on the range of the α-particle from this element. It should also be noted that thorium C does not fit the thorium curve nor does the energy of its α-particle agree with calculation. If we take $n=24{\cdot}5$ instead of 24 for this element, it fits more closely the thorium curve.

It is, of course, doubtful whether these curves can be extrapolated to give with any certainty the period of transformation corresponding to the long range α-particles from radium C and thorium C. If we extrapolate the Ur-Ra curve, the estimated period of transformation of radium C is much shorter than that deduced from the recent experiments of Jacobsen and Barton. It may be that the relation between λ and n is not so simple as that postulated here, but the rule has I hope some fundamental significance in connecting the average life of the quantum orbit with its quantum number.

The unknown value of λ for Ur II can be deduced from the Ur-Ra curve. Since its rays are characterized by $n=19{\cdot}5$, while for ionium $n=19{\cdot}0$, the half-value period should be less than that of ionium and about 100,000 years.

§ 9. *Origin of the gamma rays.*

During the last few years, notably due to the work of Ellis, Ellis and Skinner, Meitner, Thibaud, and Black, a detailed study has been made of the β-ray spectra of radioactive bodies and the frequency of the stronger gamma rays have been deduced. The general evidence indicates that the majority of these γ-rays, some of which have an individual energy of more than 2 million volts, have their origin in the nucleus of the atom, and Ellis has postulated

a system of energy levels in the atom to explain the numerical relations between the stronger gamma rays. The actual mode of excitation of these high frequency gamma rays has already been a matter of doubt. Since the most intense gamma rays usually appear in a β-ray transformation, it was natural at first to suppose that they originated from quantum jumps of electrons in the nuclear system. The possibility, however, that they may be due to movements of massive positively charged particles in the nucleus has often been suggested. The result of recent theoretical investigation, particularly of Kuhn *, seems definitely to exclude the movements of the electron as a source of the gamma rays, for Kuhn has shown on general grounds that if the gamma rays originated from high speed electrons they would not give sharp lines, as are experimentally observed, but broad diffuse bands. On the other hand, as Kuhn points out, if the gamma rays had their origin in the quantum transitions of massive positive particles, this objection would not apply.

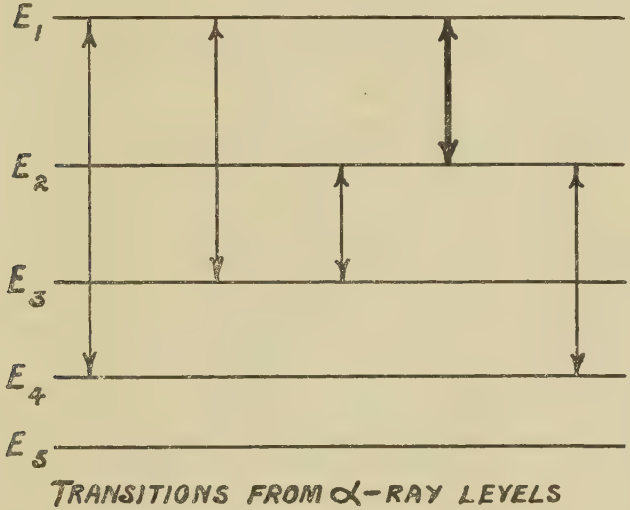
Since in our theory of the origin of the α-particles, we have postulated a number of neutral satellites which circulate in quantum orbits round the nucleus, it is of interest to consider whether the γ-rays have their origin in transitions of the satellite from one quantum level to another. Such a view is not obviously contradicted by the facts, for it is known that not only do γ-rays arise in many cases after β-ray transformations but also in a number of cases, notably radium, actinium X and radioactinium, the emission of γ-rays either accompanies or follows transformations in which only α-particles are emitted.

We may suppose in a general way that as a result of the violent disturbance which follows the emission of an α or β particle from the nuclear structure, one of the satellites becomes unstable, but instead of being ejected from the nucleus drops from one quantum level to another, radiating during the process the difference in the energies of the satellite in equilibrium in these two quantum states. There are a number of possibilities to be considered which are illustrated in the following diagram (fig. 3). Suppose the α satellite in the level E_1 becomes unstable. Considering a large number of atoms some of the satellites may fall to the level E_2, others to the level E_3 and so on. These will give rise to γ-rays of frequency ν given by $h\nu_1 = E_1 - E_2$, $h\nu_2 = E_1 - E_3$ etc. The relative number of γ-ray quanta of each frequency depends on the probability of each of these transitions. There is also another possibility to consider.

* *Zeit. f. Phys.* xliii. p. 56, 1927 ; xliv. p. 32, 1927.

After the transition for example E_1 to E_2 the satellite may be only momentarily stable, and after a short interval fall again to lower levels E_4, E_5 etc., emitting corresponding γ-rays in the process. It may also happen that more than one satellite may become unstable owing to the disturbance so that two or more systems of γ rays may arise.

Fig. 3.



TRANSITIONS FROM α-RAY LEVELS

From comparison of the theory with the energy of emission of α-particles, we have provisionally fixed the energies of the possible quantum levels where α satellites are involved. The energies of some of these levels have been given in Table II. The energy of the possible levels for a radioactive atom of any nuclear charge can be calculated from equation 11. Since, as far as our evidence goes, all levels are possible in the radioactive elements between n about 8 or 10 and $n=30$ or more, including half quanta, there are a large number of possible transitions to select from.

In considering possible transitions, it must be borne in mind that only a few of the possible levels are occupied by satellites even in the parent element uranium, and in the course of its successive transformations a number of these satellites have been removed. Consequently in an atom like radium C, there may be a number of vacant levels in the system which may be occupied either permanently or momentarily by the satellite in its transition.

From consideration of these energy levels, it is at once clear that the differences of the energies in a transition from one level to another are of the right order of magnitude to include not only the γ-rays of highest energy—about 3 million volts—but also by transitions between the lower levels to account for the emission of γ-rays of much lower energy—about 100,000 volts—which are strongly represented in certain γ-ray bodies.

In endeavouring to account for any particular system of γ-rays, we are faced with the difficulty that among such a large group of possible levels, a number of approximate coincidences within experimental error are found between the observed energy of the γ-rays and the energy differences between various levels. In order to guide us in the correct choice, we require to know not only the vacant levels but, from optical analogy, the principles of selection between possible transitions. For example, can transitions occur only between quantum numbers of the same kind whether integral or half quantum numbers? In searching for such criteria, it is clear that a knowledge not only of the frequency of the γ-rays but of their relative intensity is of great importance. For example, it does not seem likely that a weak γ-ray which arises from a transition $E_1 \rightarrow E_2$ could give rise to a γ-ray of stronger intensity due to a transition $E_2 \rightarrow E_3$ and so on. By taking into account the intensities of the γ-rays, the choice of possible levels is obviously much restricted.

I have found that it is possible in these ways to find a scheme of transitions that fits in many cases reasonably well, and, in some cases surprisingly well, with existing γ-ray data. I hope in a subsequent paper to give examples of the agreement between theory and observation. Before, however, any definite decision can be made on the adequacy of this theory of the origin of the γ-rays, it will be necessary to analyse and study in detail the large amount of γ-ray data available for a number of the radioactive elements. The general evidence is, however, sufficiently strong to warrant a very close examination to test the validity of this theory which connects together in such a simple way the two main types of radiation from the radioactive elements.

§ 10. *Structure of the atom.*

On the views put forward in this paper, the nucleus of a heavy atom has certain well defined regions in its structure. At the centre is the controlling charged nucleus of very

small dimensions surrounded at a distance by a number of neutral satellites describing quantum orbits controlled by the electric field from the central nucleus. Some years ago I suggested that the central nucleus was a closely ordered, semi-crystalline arrangement of helium nuclei and electrons. Whatever views may be taken on this point, it is fairly certain that the central nucleus of a heavy element is a very compact structure, occupying a volume of radius not greater than 1×10^{-12} cm. The region around the central nucleus extending to about $r = 1{\cdot}5 \times 10^{-12}$ cm. is probably occupied by electrons and possibly also charged nuclei of small mass which are held in equilibrium by the attractive forces which arise from the distortion or polarization of the central nucleus. The electrons in this region, circulating round the nucleus, must have velocities close to that of light.

The comparatively large region between $r = 1{\cdot}5 \times 10^{-12}$ to about 6×10^{-12} cm. may be occupied by a number of neutral satellites held in equilibrium by the polarizing action of the electric field arising from the central nucleus. In the case of the radioactive atoms, we have seen that the satellites must consist in part of neutral helium nuclei which lose their closely bound electrons when the electric field falls below a certain critical value. No definite information is so far available as to the number of these satellites surrounding the nucleus or whether the satellites are all of the same kind. From a study of the relative masses of the isotopes by Aston, it seems not unlikely that neutral satellites of mass 2 or mass 3 and possibly even of mass 1—neutrons—may exist in the strong electric fields of the central nucleus. The radioactive evidence does not help us in this question as only helium nuclei are ejected in the transformations. On the other hand, in the artificial disintegration of elements by bombardment with α-particles, only protons of mass 1 are ejected, but it is difficult to be certain whether the proton which is ejected exists in the nucleus as a charged particle or as part of an electrically neutral combination held in equilibrium at a distance by polarizing forces. It may be that a closer study of the frequency of the disintegrations and the energy of the protons expelled from different elements may throw further light on this question.

We have not so far discussed the important problem whether a central nucleus of identical charge and mass is common to a number of elements or whether it varies regularly in charge and mass from atom to atom. If the central nucleus is a closely ordered and almost crystalline arrangement of its component electrons and protons, it may

be that the number of such stable arrangements is limited in number, and that a given central nucleus may be common to a number of elements. On the theory advanced in this paper, all of the elements belonging to one particular radioactive series have a common nucleus, and it is quite likely that some of the heavier ordinary elements, lead, bismuth and thallium for example, belong to the same nuclear system.

It is of interest to consider the range of atomic number for which α satellites can exist. Taking into account the data given in § 5, it can be shown that for a nuclear charge 84, the innermost orbit corresponding to an 11·3 cm. α-particle and the outermost orbit corresponding to the α-particle from Ur I are included between $r = 1{\cdot}9 \times 10^{-12}$ and $4{\cdot}5 \times 10^{-12}$ cm. Supposing that helium satellites can only exist within the range of electric fields corresponding to these distances, it can be shown, disregarding all questions of stability, that α-satellites are possible but unlikely for atomic number Z as low as 15 and from analogy with the radioactive series should become numerous for Z about 30. It may be significant that the average number of isotopes of the elements increase in a marked manner after about $n = 29$.

Unfortunately we have no corresponding information to estimate when a nucleus can attach a satellite of mass 2, which from isotopic evidence appears to play an important part in nuclear structure. It seems likely that neutral satellites are important constituents of all elements of atomic number greater than 30, but probably cannot exist as a constituent of the very light elements.

We can form the following picture of a radioactive atom. One of the neutral α satellites, which circulates in a quantized orbit round the central nucleus, for some reason becomes unstable and escapes from the nucleus losing its two electrons when the electric field falls to a critical value. It escapes as a doubly charged helium nucleus with a speed depending on its quantum orbit and nuclear charge. The two electrons which are liberated from the satellite, fall in towards the nucleus, probably circulating with nearly the speed of light close to the central nucleus and inside the region occupied by the neutral satellites. Occasionally one of these electrons is hurled from the system, giving rise to a disintegration electron. The disturbance of the neutral satellite system by the liberation of an α-particle or swift electron may lead to its rearrangement, involving the transition of one or more satellites from one quantum orbit to another, emitting in the process γ-rays of frequency determined by quantum relations.

The question whether the γ-rays originate in such quantum transitions of the α satellites as we have outlined is difficult to determine with certainty but the evidence, so far available, does not contradict such an hypothesis. Before more progress can be made it will be necessary to determine the possible energy levels of the satellite system with precision, and on the present theory this will involve a much more accurate determination of the energies of the α-particles expelled in each transformation. At the same time, the frequency of the main γ-rays and their intensities will be required to be known with the utmost precision. In this way, valuable data will be available to test any working hypothesis of the origin of the α and γ rays in radioactive transformations, and thus to help in throwing light on the general problem of the structure of atomic nuclei.

Cavendish Laboratory,
Aug. 10, 1927.

LII. *The Scattering of α-particles by Helium.* *By* Prof. Sir E. Rutherford, *O.M., P.R.S., Cavendish Professor of Experimental Physics, and* J. Chadwick, *Ph.D., F.R.S., Fellow of Gonville and Caius College, Cambridge* *.

THE study of the collisions of α-particles with hydrogen nuclei has shown that the force between the α-particle and the H nucleus obeys Coulomb's law for large distances of collision, but that it diverges very markedly from this law at close distances. The experiments of Chadwick and Bieler † showed that for distances of collision less than about 4×10^{-13} cm. the force between the two particles increased much more rapidly with decrease of distance than could be accounted for on an inverse square law of force. For example, in one series of experiments the H particles were observed which were projected after collision in directions making angles from 20° to 30° with the direction of the colliding α-particle. When the incident α-particle had a range in air of less than 2·0 cm., the number of H particles projected in this specified direction was about that to be expected if the force between the particles was given by Coulomb's law. With incident α-particles of greater range than this the number of H particles observed became greater than the theoretical number, and the discrepancy rose very

* Communicated by the Authors.
† Chadwick & Bieler, Phil. Mag. xlii. p. 923 (1921).

rapidly as the velocity of the α-particle was further increased. With α-particles of 2·9 cm. range the observed number of H particles was three times the number calculated on inverse square forces, while with α-particles of 6·6 cm. range the observed number was thirty times the calculated number. Not only was the number of H particles projected at small angles by α-particles of high velocity greatly in excess, but the observed variation of the number of H particles with the velocity of the α-particle was in the opposite direction from that predicted by the simple theory.

This divergence from the predictions based on the assumption of Coulomb forces was interpreted by Chadwick and Bieler in the following way. Assuming that the H nucleus could be regarded as a point charge, a model was sought for the He nucleus or α-particle which would account in a general way for all the experimental results. It was shown, by comparison with Darwin's calculations, that the α-particle behaved in these collisions as a body with properties intermediate between those of an elastic sphere and an elastic plate, and it was compared, as a first approximation, with an elastic oblate spheroid of semi-axes about 8×10^{-13} cm. and 4×10^{-13} cm., moving in the direction of its minor axis. A H nucleus projected towards such an α-particle would move under the ordinary electrostatic forces given by Coulomb's law until it reached a spheroidal surface of the above dimensions. It would there encounter a very powerful field of force and recoil as from a hard elastic body. While such a model of α-particle accounted in a rough way for the experimental observations, it was not found possible to obtain a very close comparison owing to the difficulty of calculating the collision relations for an oblate spheroid.

A further line of attack on this question of the field of force in the immediate neighbourhood of the He nucleus can be obtained by the investigation of the collisions of α-particles with helium nuclei. In this case both particles concerned in the collision have the same structure. There is therefore no need to assume a structure for one nucleus in order to deduce that of the other, as was done in the case discussed above.

If E, M, V are the charge, mass, and initial velocity of the α-particle concerned in the collision, v its velocity after impact with the He nucleus at rest, and u the velocity of the He nucleus set in motion by the collision, we have, on the assumption that energy is conserved in these collisions,

$$u = \mathrm{V}\cos\theta, \qquad v = \mathrm{V}\cos\phi, \qquad \phi = \pi/2 - \theta,$$

where θ, ϕ are the angles made by the lines of motion of the He nucleus and the α-particle after collision with the initial line of motion of the α-particle.

The assumption that in these collisions the energy is conserved in the translational motion of the particles is amply justified by the experiments of Blackett *. Blackett has obtained Wilson photographs of the collisions of α-particles with He nuclei, in which he has been able to measure accurately the directions of motion of both particles after impact. He finds that the angle $(\theta+\phi)$ is very close to a right angle, the result to be expected for a perfectly elastic collision between two particles of equal mass, one of which is initially at rest.

If we allow a pencil of α-particles to pass through helium and place a zinc sulphide screen in such a way that the particles falling on it travel at an angle ϕ to the direction of the pencil, the scintillations observed on the screen will be due not only to the α-particles scattered through the angle ϕ, but also to those He nuclei set in motion in this direction. The velocities of the particles of both types will be the same, $V\cos\phi$, or the ranges, $R\cos^3\phi$, where R is the range of the incident α-particle. There is therefore no means of distinguishing between a scattered α-particle and a projected He nucleus. The two types correspond, in general, to collisions of different kinds, for the He nuclei projected at an angle ϕ are the companions of the α-particles scattered through an angle $\pi/2-\phi$. When $\phi=45°$, however, both sets of particles arise from the same type of collision.

If we assume that the forces between the particles are given by Coulomb's law, the numbers of the scattered α-particles and the projected He nuclei can be easily calculated. If the α-particle approaches initially along a line at a perpendicular distance p from the He nucleus, it can be shown that

$$p = \tan\theta \cdot \frac{E^2}{V^2} \cdot \frac{2}{M},$$

and the closest distance of approach during the collision is

$$\frac{E^2}{V^2} \cdot \frac{2}{M} \cdot (1+\sec\theta).$$

If Q be the number of α-particles per second in the incident pencil, and ω the solid angle subtended by the ZnS screen

* Blackett, Roy. Proc. Soc. A, cvii. p. 349 (1925).

placed at an angle ϕ, then the number of α-particles scattered to the screen is

$$Q\, nt\, \omega \frac{1}{V^4} \cdot \frac{E^4}{M^2} \cdot 4 \cot \phi \operatorname{cosec}^3 \phi,$$

where n is the number of He atoms per c.c. and t is the length in cm. of the scattering path.

The number of He atoms set in motion in the direction ϕ under the same conditions is

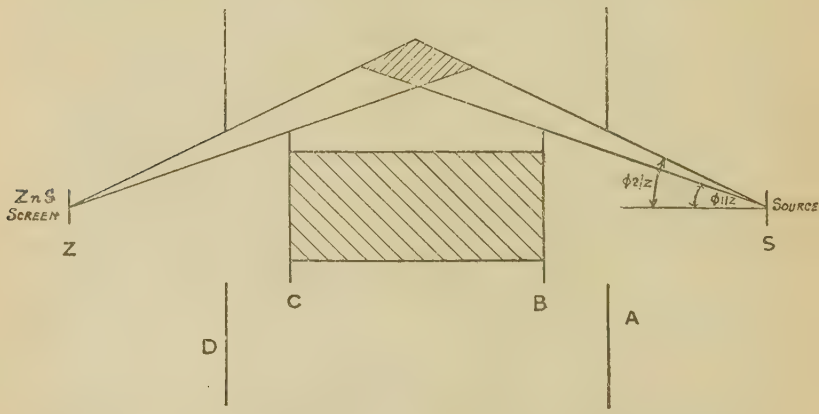
$$Q\, nt\, \omega \frac{1}{V^4} \cdot \frac{E^4}{M^2} \cdot 4 \sec^3 \phi.$$

The total number of particles received on the ZnS screen is the sum of these two numbers.

Experimental Method.

The arrangement used in these experiments was the same in principle as that used by Chadwick * for measurement of the scattering of α-particles by metal foils. In the present case we had to deal with scattering in a gas, and certain modifications were made in the arrangement of diaphragms.

Fig. 1.



In all, four diaphragms were necessary, as shown at A, B, C, and D in fig. 1. The diaphragms A and D consisted of graphite sheets containing circular holes, while diaphragms B and C were small graphite disks. A and B served to define the incident beam of α-particles, an annular ring of limits $\frac{1}{2}\phi_1$ and $\frac{1}{2}\phi_2$, proceeding from the source S, and C and

* Chadwick, Phil. Mag. xl. p. 734 (1920).

D defined the scattered beam received by the zinc sulphide screen Z. The scattering apparatus was on a small scale, and it was necessary to machine and align the parts accurately. The volume of gas which is effective in scattering particles to Z is an annular ring, shown shaded in the figure. If the gas used is helium, the number of α-particles scattered per second to unit area of the ZnS screen is given by

$$\frac{Q\,nt\,b^2}{16r^2}\,(\mathrm{cosec}^2\,\phi_1-\mathrm{cosec}^2\,\phi_2),$$

where r is the mean distance from the source to the scattering region, and $b=\dfrac{2E^2}{MV^2}$.

Similarly, the number of those He nuclei which are projected by a collision with an α-particle so as to reach unit area of the screen Z per second is

$$\frac{Q\,nt\,b^2}{16r^2}\,(\sec^2\,\phi_1-\sec^2\,\phi_2).$$

These latter particles correspond to the α-particles scattered between angles $90°-\phi_1$ and $90°-\phi_2$. The observations carried out within the angular limits ϕ_1 and ϕ_2 measure therefore the scattering within two sets of limits situated at equal intervals from 45°. It is consequently impossible to deduce without ambiguity the complete angular distribution of the α-particles scattered by helium nuclei, for, as has been pointed out, we have no means of distinguishing a scattered α-particle from a projected He nucleus. In some cases, however, even where the law of inverse square is no longer applicable, it is possible to form a rough estimate of the relative importance of the two groups of particles. In the experiments described in this paper we have not attempted to cover the whole range of scattered particles, but we have restricted our attention to the scattering within certain selected angular intervals and we have examined in each region the variation of the scattering as the velocity of the incident α-particles was varied.

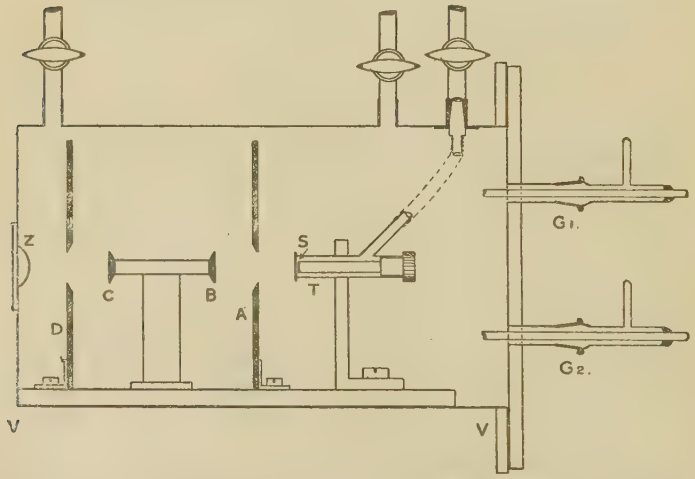
The apparatus employed is shown in fig. 2. The source and diaphragms were carried on a brass plate which fitted into slides fixed to the base of the brass vessel VV. The source, a small disk of 3 to 4 mm. diameter, was enclosed in the brass tube T, the end of which was covered with a thin film of collodion. The diaphragms A and D were mounted on short brass supports, while B and C were attached to the

ends of a lead cylinder of the appropriate length. This cylinder was carried by a thin plate of graphite fixed by means of wax to the brass carrier. The source, the four diaphragms, and the zinc sulphide screen were centred on a common axis.

To reduce extraneous scattering to a minimum, all surfaces exposed to the α-particles emitted by the source were covered, as far as possible, with sheets of pure graphite. In addition, the disks B and C had, in each series of experiments, a diameter at least equal to that of the apertures of diaphragms A and D. Scattering from the edges of the diaphragms to the screen was then usually of very small amount.

The disturbing effect of "contamination" was guarded against by placing the source in the closed tube T. The

Fig. 2.



amount of contamination could be determined at any time during the experiment by rotating in front of the source a graphite disk carried by the ground joint G_1. The α-particles were then cut off from the scattering region and the scintillations observed on the screen were due to the natural effect together with the contamination effect.

By means of a second ground joint G_2 an absorbing sheet of mica could be introduced in the path of the incident α-particles. In this way the scattering of α-particles of two different ranges could be compared in the course of one experiment. Further changes in the range of the incident α-particles were made by placing sheets of mica directly over the end of the tube T, in addition to the fixed collodion film.

The source of α-particles was, in most experiments, the active deposit of radium, obtained in the usual way on the brass disk S. In some cases where α-particles of greater range than 7 cm. were required, thorium active deposit was used After fixing the source in the tube T and placing the carrier holding the diaphragms in position, the box VV was slowly evacuated. The amount of extraneous scattering was then determined by counts of the number of scintillations appearing on the screen Z. Pure helium was then admitted into the box through a long U-tube cooled in liquid air, and the observations of the scattering in this gas were made.

Results.

The results obtained in these experiments are collected in the following tables. The first column gives the mean range of the incident α-particle at the point of scattering, the second column the observed number of scattered α-particles and projected He nuclei per mgm. activity of the source, and the third the corresponding number to be expected on the assumption of inverse square forces. The fourth column gives the ratio of the observed number to the inverse square number.

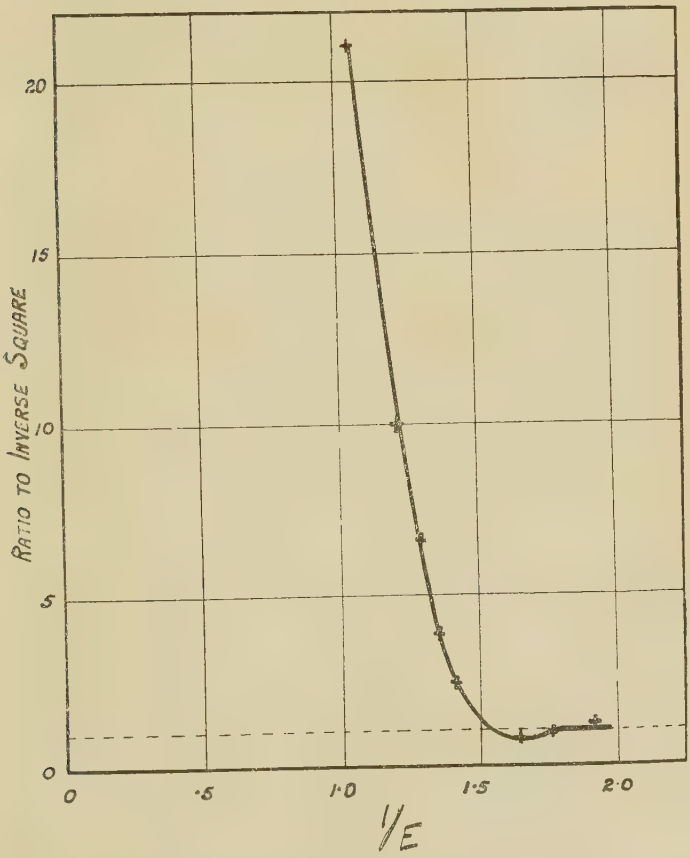
The number of particles which should be observed if the collisions were governed by inverse square forces was arrived at, for each series of experiments, in two ways: first by calculation from the geometry of the arrangement, and secondly, by observation of the number of α-particles scattered by argon under the same conditions as in the helium experiments. For this purpose the vessel VV was evacuated and filled to a suitable pressure with pure argon. It was assumed that, for the angles of scattering dealt with in these experiments, the forces between the α-particle and the argon nucleus obey Coulomb's law. In the series of experiments at the larger angles of scattering the numbers of scattered particles observed with argon agreed very closely with those calculated from the geometry of the experimental arrangement. At the very small angles of scattering obtaining in some of the experiments the agreement was not so good, and in one case the observed numbers were 15 per cent. higher than the calculated number. In the calculation it was assumed that the source and screen were of dimensions small compared with those of the diaphragms. In the experiments dealing with small angles this was no longer the case, and the discrepancy mentioned above was attributed to this cause. In the following tables

Range of α-particles in cm. of air.	Number of particles. Observed.	Calculated.	Ratio.
	Scattering angles 40° to 50°.		
6·35	4·4	·21	21
5·3	2·65	·26	10
4·75	2·05	·31	6·6
4·4	1·3	·34	3·9
4·15	·83	·36	2·3
3·3	·44	·49	·9
3·0	·7	·6	1·2
2·6	·95	·7	1·3
	Scattering angles 29° to 44°.		
8·0	10	·53	19
6·3	6·6	·72	9
5·1	4·2	·96	4·4
4·5	1·7	1·14	1·5
3·0	2·2	1·95	1·1
2·3	3·0	2·8	1·1
	Scattering angles 10° to 20°.		
6·05	9·3	5·13	1·81
5·3	8·2	6·12	1·34
4·8	7·3	6·96	1·05
4·0	4·6	8·86	·52
3·2	4·0	12·0	·33
2·7	5·7	15·2	·38
	Scattering angles 8° to 12°.		
6·0	1·3	1·43	·91
4·7	·9	1·97	·46
3·9	·6	2·52	·24
2·6	2·4	4·34	·55
1·9	4·2	6·56	·64
	Scattering angles 4° to 7° 30′.		
5·6	1·9	3·1	·61
4·65	1·9	3·96	·48
3·9	4·6	5·0	·92
3·5	6·4	5·8	1·1
3·1	6·8	6·8	1·0
2·75	9·5	8·0	1·2
	Scattering angles 4° to 6°.		
5·65	1·37	1·90	·72
4·7	1·95	2·45	·8
3·6	3·5	3·48	1·0
3·15	3·7	4·16	·9
2·6	6·5	5·5	1·2

the inverse square numbers are therefore deduced from the comparison experiments with argon, rather than from calculation directly from the dimensions of the apparatus.

The results obtained when the particles were observed between the angles of 40° and 50° are shown in the curve of fig. 3, where the ordinates represent the ratio of the

Fig. 3.



observed to the calculated number, and the abscissæ the value of 1/E, where E is the energy of the incident α-particles. The dotted line for ordinate unity thus represents the relation that would be observed for an inverse square law of force. The ratio is large for the swifter α-particles, falls rapidly to a value just below unity as the

energy of the α-particle decreases, and rises again to about the calculated value. Since within this range of angles the scattered α-particles and the helium nuclei set in motion by recoil are equal in number, this curve also represents the actual variation in number of the projected He nuclei for different speeds of the colliding α-particle. If we compare this curve with the data given by Chadwick and Bieler for the variation in number of project H nuclei between 21° and 31° with the speed of the incident α-particle, we find a marked similarity, not only in the general shape, but also in the magnitude of the divergence from the calculated numbers. Agreement with the calculated numbers is reached at approximately the same conditions in both types of collision.

Taken as a whole, the results given in the above tables indicate that the distribution of projected particles in collisions between α-particles and He nuclei is very similar to that observed when α-particles collide with H nuclei. There is no doubt that, if it were possible to separate the projected nuclei from the scattered α-particles, we should find a similar concentration in the forward direction, which is the more marked the swifter the incident α-particle.

As we have previously remarked, it is not possible to deduce from these experiments the relations between the number of projected He nuclei, the angle of projection, and the speed of the colliding α-particles, as can be done for the collisions in hydrogen. We are to a certain extent limited to finding at what distance of approach between the α-particle and the He nucleus the numbers of projected nuclei plus scattered α-particles become abnormal, for different angles of collision. In this respect the investigation is easier than for collisions in hydrogen, for a wider range of angles is experimentally possible. For example, it was a comparatively simple matter to find the expected deficiency in the number of projected + scattered particles between certain angles of collision, which is the necessary consequence of the excess scattering at other angles *. If we consider the collisions of α-particles of fixed initial velocity, we should expect to find, for very small angles of scattering or angles of projection of the He nucleus close to 90°, that the numbers of particles are normal. As the angle of scattering is increased the numbers should at some angle fall below the inverse square number to a minimum and

* *Cf.* Rutherford, Guthrie Lecture, Proc. Phys. Soc. Lond. xxxix. p. 359 (1927).

then rise sharply for the larger angles. The experiments on collisions in hydrogen dealt mainly with the excess scattering, and it was difficult experimentally to investigate the regions in which the number of particles should fall below the calculated number, but the present results show this phenomenon very clearly for the collisions of α-particles of 3 to 4 cm. range.

From the above results we are able to make an approximate estimate of the dimensions of the region over which the forces between the α-particle and the He nucleus become normal. Considering the experiments between 40° and 50°, it appears that the forces are given by Coulomb's law when the incident α-particle has a range of less than about 3 cm., that is, until the distance of approach between the centres of the particles becomes less than about $3{\cdot}5 \times 10^{-13}$ cm. It is obvious, even from this one series of experiments, that the region of abnormal forces is not spherical, for a comparison of the curve of fig. 3 with the corresponding curve calculated for an elastic sphere, gives a radius for the sphere varying from about $3{\cdot}5 \times 10^{-13}$ cm. for the collisions of slow α-particles to about 8×10^{-13} cm. for the fast α-particles. We must conclude, as in the case of the hydrogen collisions, that the region of abnormal forces has a plate-like shape. This indication is strongly confirmed by the experiments at smaller angles of scattering. At these angles the number of projected particles is, if inverse square forces hold, small compared with the number of scattered particles. For example, between 8° and 12° the number of scattered particles should be 108 times the number of projected particles. It is therefore reasonable to assume that, except in the collisions of very fast α-particles, we are here observing mainly the scattered particles and that the projected particles are not important. The experiments at these small angles show a common trend. As the velocity of the α-particle is decreased, the ratio of the number of particles observed to the calculated first falls, sometimes to as low as one-third, and subsequently rises to approximately unity. The investigations at these angles thus deal rather with a deficiency in scattering than with an excess. The same departure from inverse square forces is, however, responsible both for the deficient scattering observed here and for the excess scattering observed at other angles. When we calculate from these experiments the distance of approach between the centres of the colliding particles at which inverse square numbers are finally reached, we find that this distance is much greater than that obtained from the

collisions between 40° and 50°, being about 12 to 15×10^{-13} cm.

It thus appears that for central collisions between an α-particle and a He nucleus the law of force remains normal so long as the distance of approach between the centres of the particles is greater than about $3{\cdot}5 \times 10^{-13}$ cm., while for glancing collisions the distance of approach must not be less than about 14×10^{-13} cm. In the collisions of the α-particle with H nuclei the corresponding dimensions of the region of abnormal forces were estimated to be about 4×10^{-13} cm. and 8×10^{-13} cm. The plate-like form of this region is therefore even more apparent in the helium collisions than in the hydrogen collisions.

Discussion.

In this examination of the results we have compared the observed numbers of scattered α-particles and projected nuclei with the numbers to be expected if the forces between the particles are given by Coulomb's law and on the assumption that the rules of classical mechanics are valid. Any divergence from the calculations has been assigned to a departure from the Coulomb law of force.

During the last year the adequacy of classical mechanics to interpret atomic phenomena has been questioned, and a new mechanics has been developed by Heisenberg, Schrödinger, Born, Dirac, and others. The power of this new mechanics has already been demonstrated by the solution of a number of atomic problems, and it has been suggested that the abnormal scattering of α-particles by light elements may be due rather to the failure of the classical mechanics in dealing with such close collisions than to any departure from the inverse square law of force. Recently, however, Oppenheimer* has shown that on certain assumptions the laws of scattering by a central field of force varying as the inverse square have the same form on the new mechanics as on classical mechanics. It appears unlikely that the large divergences observed in the present experiments and in the previous experiments with hydrogen can be explained solely on the basis of the new mechanics. Some departure from the Coulomb law of force is thus indicated. It might still arise that the peculiar distribution of scattering observed was then a consequence of a central field of force, not that of the inverse square, combined with the wave mechanics. Certain criteria have been given by Schrödinger and de Broglie for

* Oppenheimer, *Zs. f. Phys.* xliii. p. 413 (1927).

the conditions under which marked diffraction patterns may be expected to appear in the collisions of particles. These criteria have been interpreted by Blackett * in terms of collision relations founded on classical mechanics, but unfortunately they are not precisely defined, and until some scattering phenomena have been completely explained in this way, so as to furnish the requisite comparative data, it is difficult to decide where diffraction patterns may be expected to disclose themselves in collisions of the type considered here.

It seems reasonable then to ascribe the abnormal scattering of α-particles by hydrogen and helium mainly to a departure from inverse square forces, and to seek an explanation of the plate-like shape of the surface at which this departure occurs in the structure of the nuclei concerned in the collision. The experimental results can be explained in a general way if we introduce a force which increases very rapidly as the distance of collision decreases. This force may be either attractive or repulsive. Such a force was postulated by Chadwick and Bieler to account for the hydrogen collisions, but no evidence of the form or nature of the force was obtained. In order to explain his observations on the scattering of α-particles by aluminium, Bieler † was led to assume that the α-particle was acted on, in addition to the Coulomb force of repulsion, by a force of attraction varying as the inverse fourth power of the distance. By this means he was able to account approximately for his experimental results. More recently, Debye and Hardmeier ‡ have suggested that the additional attractive force can be derived from the assumption that the aluminium nucleus consists of charged particles. They suppose that as the α-particle approaches closely to the nucleus there will arise a polarization of the nucleus in the same way as a charged particle in approaching a neutral atom is able to polarize its structure. This polarization will cause an attractive force on the α-particle, which, if the charged particles of the nucleus are held together by inverse square forces, will vary as r^{-5}, where r is the distance from the centre of the nucleus. With reasonable assumptions about the constants involved, Debye and Hardmeier (and later Hardmeier § in great detail) calculated the scattering by aluminium on this basis, and showed that the experimental results of Bieler and of the present authors could be

* Blackett, Proc. Camb. Phil. Soc. xxiii. p. 698 (1927).
† Bieler, Proc. Camb. Phil. Soc. xxi. p. 686 (1923).
‡ Debye and Hardmeier, *Phys. Zeit.* xxvii. p. 196 (1926).
§ Hardmeier, *Phys. Zeit.* xxviii. p. 181 (1927).

explained. However fruitful this idea may prove in other cases, it does not seem possible to explain the collisions with hydrogen or helium nuclei without some additional assumption about the "shape" of the α-particle. The most striking fact which appears from our experiments is that while for central collisions the departure from inverse square forces occurs at a distance of about $3{\cdot}5 \times 10^{-13}$ cm. between the centres of the particles, for glancing collisions the departure occurs at about 14×10^{-13} cm. At this distance the normal forces are relatively small, and any distortional or polarizing forces must be correspondingly small unless the nuclei are supposed to have a greater dimension in this direction than in the direction at right angles.

Whatever may be the origin of the rapidly varying forces acting in close collisions, it appears necessary to assume some plate-like "shape" for the α-particle, that is for the region around the α-particle where these forces become evident. A similar assumption was made by Chadwick and Bieler to explain their experiments on collisions in hydrogen. Regarding the H particle as a point charge, they deduced that the abnormal forces came into action over a spheroidal surface of semi-axes 8×10^{-13} cm. and 4×10^{-13} cm., the short axis being in the line of motion of the α-particle. From the present experiments, where the α-particle collides with a He nucleus, we should expect to find that the forces become abnormal over a region of about twice these dimensions. For glancing collisions in helium the critical distance is, as we have seen, about 14×10^{-13} cm., or roughly twice the major axis of the above spheroid. For the central collisions, however, the distance is about $3{\cdot}5 \times 10^{-13}$ cm., actually rather less than the corresponding critical distance for the collisions in hydrogen. Although it is difficult to form any estimate of the effects of distortion, it would appear that the H nucleus or proton must have dimensions comparable with those of the α-particle. This is an unexpected result, for it is usually supposed that the proton has a radius of about 10^{-16} cm. It would, however, be more accurate to say that the region around the proton where the forces are abnormal is comparable in size with the corresponding region for the α-particle, for we can conclude from our experiments nothing about the volume occupied by the actual structure of the nucleus. Allowing for the "size" of the H particle, we may bring the hydrogen and helium results into some rough agreement by assuming that the "shape" of the α-particle is a spheroid of semi-axes about 7×10^{-13} cm. and 2×10^{-13} cm. moving with the short axis in the line of the

motion of α-particle. The assumption of a definite orientation of the α-particle which was made in the interpretation of the hydrogen collisions, though no adequate proof was obtained, is also suggested by the experiments in helium. Here, indeed, it seems almost necessary to assume further that the helium nucleus does not present all possible orientations in the collisions, and to suppose that the abnormal forces also provide a turning couple controlling the relative orientations of the colliding nuclei.

Any explanation of the origin of the forces which are brought to light by these studies of collisions must necessarily be very tentative in character, for it must be remembered that the nuclei are both in motion during the collision and both are in an abnormal state owing to the powerful distorting forces arising from their close approach to each other. It seems unlikely that the usual electrostatic forces, even when modified by the effects of distortion, could provide over such an extensive area forces of the magnitude necessary to explain the observed results. It may perhaps be suggested that the predominant part in these close collisions is the action of magnetic forces. If, as has been suggested in recent years, the electron has a definite magnetic moment associated with it, it is not unreasonable to suppose, with Frenkel *, that the proton also has a magnetic moment. The assumption of such magnetic forces does, indeed, help to explain some of the observed phenomena, though many grave difficulties still remain. Whatever we assume about the intrinsic magnetic moment of the helium nucleus, it is not difficult to show that the effect of the magnetic forces will become prominent at distances of the order of 4×10^{-13} cm., roughly the distance at which the collisions of α-particles in helium and hydrogen become abnormal. The magnetic forces will also increase very rapidly as the distance of approach decreases. It is further interesting to note that, since the deflecting force of a magnetic field on a charged particle is proportional to the speed of the particle, we are able to see in a general way why the abnormality in the scattering of α-particles increases so markedly with rise in velocity of the α-particle. It seems possible that these magnetic forces would be of the right order of magnitude, and the turning couple due to the interaction of the magnetic fields of the two nuclei offers perhaps an explanation of the apparent orientations of the particles during the collisions.

* Frenkel, *Zs. f. Phys.* xxxvii. p. 243 (1926).

While this suggestion of the importance of magnetic forces around nuclei appears to offer a qualitative explanation of our experimental results, the detailed calculation of their effects is very difficult and perhaps, in the present state of our information about the structure of nuclei, somewhat premature.

Summary.

The collisions of α-particles with helium nuclei have been investigated. The results show that, in general, the collision relations for these particles are similar to those holding for the collisions between an α-particle and a hydrogen nucleus. At large distances of collision the forces between the particles are given by Coulomb's law, but at closer distances very strong additional forces come into action. Possible explanations of the origin of these additional forces are discussed, and it is suggested tentatively that they may be due to magnetic fields in the nuclei.

Cavendish Laboratory, Cambridge.

LIII. *Intensity Measurements of X-ray Reflexions from Fine Powders. By* J. Brentano, *D.Sc., Lecturer in Physics, Manchester University* *.

Summary.

The present paper describes an investigation of the intensity of X-ray reflexions of very fine powders of sodium chloride. The intensities were evaluated by photometric measurements made on the powder photographs of sodium chloride, which had been obtained with the type of camera designed by the author.

The intensity of X-ray reflexions by this crystal has been the subject of investigations by Bragg, James and Bosanquet, A. H. Compton, Havighurst, and others. The principal difficulty in the way of obtaining reliable data is due to the existence of extinction both primary and secondary in the crystal. In the present paper the conditions of extinction of X-ray reflexions from extremely fine powders are discussed, and it is pointed out that the only extinction effect which can occur is constant for all reflexions, but is a function of the wave-length. The conditions which have to be satisfied in order to make relative intensity measurements from powders independent of the knowledge of the coefficient of absorption and of extinction are indicated.

The method adopted for the evaluation of the photographic

* Communicated by Prof. W. L. Bragg, F.R.S.

records of sodium chloride is described. The results are compared with the determinations by other authors employing single crystals and relatively coarse powders. The measurements are in general in good agreement, but for the most powerful reflexions the present measurements give somewhat higher values indicating a small amount of primary extinction in the measurements from larger crystals. Reducing a crystal to the state of a "coarse" powder can in general be considered suitable for eliminating secondary, but not primary extinction.

IN another paper by the writer in collaboration with W. E. Dawson reference has been made to intensity measurements of X-ray reflexions obtained from extremely fine sodium chloride particles produced by a chemical reaction of chlorine gas in dry sodium methoxide. It seemed to be of interest to go into a fuller discussion of these determinations in view of the work of Bragg, James and Bosanquet *, and of A. H. Compton † on this substance. In this work the distribution of electrons of the sodium and chlorine atom is derived from measurements of the scattering of X-rays from sodium chloride for various angles. One main difficulty in such determinations comes from extinction effects, which reduce the intensities of the X-ray reflexions, in particular for small angles, which otherwise would have the greatest bearing on the results.

If we define as crystal unit a region of the crystal in which the spacing of subsequent planes is regular or the crystal perfect, this extinction depends on the size of these units and on the regularity of their orientation. Referring in particular to the work of Bragg, in which an extended crystal block was used, a most careful determination of secondary extinction (the terms primary and secondary extinction are used in the sense in which they were introduced by Darwin ‡) has been made for the various reflexions and allowance for it introduced in the calculation. Darwin has shown that no direct determination of primary extinction could be made and has suggested the way of eliminating it by observing the reflexions from particles sufficiently small to make it negligible.

* Bragg, James and Bosanquet, Phil. Mag. xli. p. 309 (1921); xlii. p. 1 (1921); Phil. Mag. xliv. p. 433 (1922).

† A general account of the work of Compton and others is given in A. H. Compton, 'X-rays and Electrons,' D. Van Nostrand & Co., New York, 1926.

‡ Darwin, Phil. Mag. xliii. p. 433 (1926). See also Bragg, Darwin and James, Phil. Mag. i. p. 897 (1926).

According to Darwin the relative reduction of intensity which the reflected beam suffers through primary extinction can be expressed for a small crystal unit by a factor

$$\frac{\tanh mq}{mq}, \quad \ldots\ldots \quad (1)$$

where m is the number of reflecting planes, and

$$q = \mathrm{N}(e^2/mc^2)\mathrm{F}\lambda^2/2\sin^2\theta,$$

(N is the number of molecules per 1 cm.^{3}, F is the effective number of scattering electrons per molecule; the other letters have the usual significance), a quantity which is proportional to the amplitude reflected from each plane. Applied to rock-salt this leads for the (200) reflexion to a maximum diameter of $2{\cdot}4 \cdot 10^{-5}$ cm. in order to reduce primary extinction to less than 1 per cent.

Compton and Freeman, Compton, Harris, Bates and MacInnes, Bearden, and Havighurst * have followed this course and carried out determinations from powdered rock-salt crystals. The powders used by these authors consisted actually of particles of considerably larger diameter measuring $1 \cdot 10^{-4}$–$2 \cdot 10^{-3}$ cm., but it was assumed that the process of grinding would break up the crystal lattice and make the actual diffracting units much smaller than the crystal particles. Our experiments on gold, where it was shown that gold powder obtained by filing gave considerable extinction, seemed to make it worth while to undertake more careful measurements of the reflexions from the rock-salt particles obtained by chemical reaction which actually approximate to Darwin's condition. The mean diameter of these particles has been found to be $5{\cdot}5 \cdot 10^{-5}$ cm., giving for the (200) reflexion the factor of primary extinction equal to 4 per cent.

A few remarks may be made on the effect of extinction on intensity measurements from powders, in particular as in some recent work these conditions seem not to have been fully considered. Primary extinction, which corresponds to the loss of intensity of the reflected beam due to interference of wave-trains diffracted from different parts of the diffracting unit, can be made negligible in the powder method by reducing the size of the particles to the limits imposed by formula (1). Secondary extinction, which corresponds to the

* Freeman and Compton, 'Nature,' cx. p. 38 (1922).
A. H. Compton, *loc. cit.*
J. A. Bearden, Phys. Rev. xxvii. p. 796 (1926); xxix. p. 20 (1927).
Harris, Bates and MacInnes, Phys. Rev. xxviii. p. 235 (1926).
R. J. Havighurst, Phys. Rev. xxix. p. 882 (1926).

weakening of the diffracted beam through encountering in different crystal units lattice planes set at the reflecting angle and in which absorption is therefore particularly great, will depend on the chance of a lattice plane having a certain orientation and on its reflecting power*. In the case of refraction from a single crystal of mosaic type, *i. e.* consisting of a number of units orientated nearly parallel one to another, this will thus depend on the regularity of the crystal and on the intensity of reflexion from the particular lattice. In the case of a powder two effects have to be considered. Secondary extinction in the individual particle, if this is of "mosaic" structure, and secondary extinction due to the X-ray encountering in succession lattice planes set at a reflecting angle situated in different particles. For a powder of particles sufficiently small to show no primary extinction the first effect can be neglected, as the minimum dimensions for a block to show secondary extinction are considerably greater than the minimum dimensions for a unit to show primary extinction.

The second effect depends on the random distribution of the powder particles, as any lattice plane can have any orientation with respect to the X-ray beam. All possible lattice planes which can reflect contribute to it according to their reflecting power and according to the multiplicity factor p, the number p giving the number of times each particular lattice is represented in the crystal. This effect is the same for all reflexions, independent of the angle through which the X-rays are deflected, but depends on the nature of the crystal, the state of the powder, and on the wave-length, since these affect the intensities of the various reflexions and also the total number of spacings which can reflect. The effect can be small for certain crystals and for certain wave-lengths, it cannot be neglected in considering a general case.

In a general way secondary extinction in a sufficiently fine powder is thus a constant for all reflexions and the crystal behaves as if its coefficient of absorption were $\mu' = \mu + \epsilon$, where μ is the ordinary coefficient of absorption and ϵ the coefficient of extinction. Therefore with a powder this interferes with a direct comparison of the incident and of the reflected beams, as all the reflected intensities are affected by extinction and the coefficient ϵ cannot be determined experimentally, except by measuring the absorption

* In the treatment of reflexion from a perfect crystal by Ewald the reflecting power can be associated with an angular range. P. Ewald, *Phys. Zeitschr.* xxvi. p. 29 (1925).

coefficient μ' for the actual powder used. This measurement is difficult and exposed to serious sources of error, as it depends on having a powder layer of known and uniform density. On the other hand, the coefficient μ' is the same for all reflexions.

For the reflexion from a flat layer of powder of such thickness to be totally absorbing, on which a beam of the angular aperture de is incident at a glancing angle α and reflected at a glancing angle β, the intensity of the reflected radiation is determined by

$$kI\frac{1}{\mu'(1+\sin\alpha/\sin\beta)}de,$$

where I is the intensity of the incident radiation and k contains those factors which do not depend on absorption and on the geometry of the apparatus. It appears thus that the effect of extinction becomes constant for all reflexions so long as $\sin\alpha/\sin\beta$ is constant. This condition is satisfied in the arrangement described by the author *, with which the records from the layers of fine sodium chloride powder were taken. In it the distance of the powder from the entrance slit of the instrument and from the film resp. the ionization chamber being a and b, the ratio $\sin\alpha/\sin\beta = a/b$ is satisfied for all angles of reflexion. Unequal distances a and b are considered, as they allow in general greater intensities to be used. By employing this method for quantitative measurements the relative values of the intensities become independent of μ', so that the coefficient of absorption need not be known †.

To test the absence of primary extinction and the allowance introduced for secondary extinction in the determinations of Bragg, James and Bosanquet, the relative values of the F curves corrected for secondary extinction calculated by Bragg can be compared with the values calculated from our measurements when using the same relation between F^2 and the reflected intensities.

The expression based on the classical scattering of the electron gives

$$F^2 \sim P\frac{\sin 2\theta \sin\theta}{p(1+\cos^2 2\theta)}\lambda^3,$$

* J. Brentano, Proc. Phys. Soc. London, xxxvii. p. 184 (1925).

† Havighurst in adopting our method seems to have overlooked this point, as in considering a case where $a \neq b$ he quotes a formula given by Compton for passing from the observed intensities to absolute values; this formula does not hold good for the conditions of the experiment.

where P corresponds to the integrated reflexion and a term $\sin\theta/p$ appears, as compared with the expression for the reflexion from a single face, in order to account for the particular conditions of the powder-method.

Bragg's determinations were carried out with Rh.Kα radiation, while we used Cu.Kα. As F is a function of $\sin\theta/\lambda$, our values have to be referred to angles θ' such that $\sin\theta'/\sin\theta=\dfrac{\lambda\,\mathrm{RhK}}{\lambda\,\mathrm{CuK}}=0{\cdot}399$, in order to make them comparable with the values obtained from rhodium radiation.

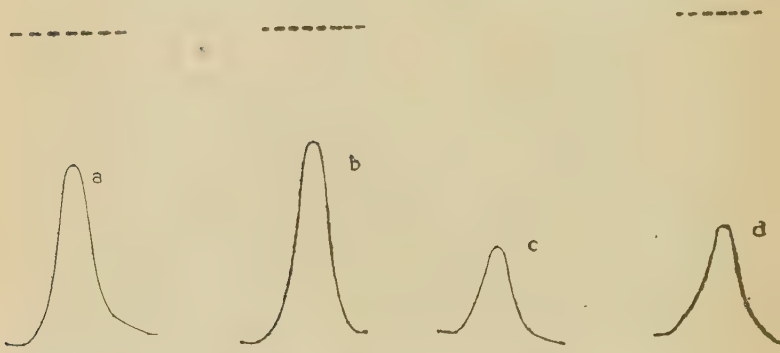
Another way of comparing the determinations is to express the relative values of F as a function of $\mathrm{H}^2=h_1^2+h_2^2+h_3^2$ (the sum of the squares of the indices of each reflexion), as the relation between the two quantities is independent of the wave-length.

The reflexions from sodium chloride were recorded photographically and a suitable procedure had to be evolved for their measurement. The blackening records obtained from a self-registering instrument of Moll were not satisfactory for this particular measurement, as the heights of the peaks seemed to be affected by the inertia of the thermopile. A photometer was therefore designed in which the film could be set in any desired position in front of a fine slit by the action of a micrometer-screw. Light illuminating the slit was allowed to fall on a thermopile connected to the galvanometer. Definite portions of the line could thus be measured with the film stationary, and the correct working of the instrument could be checked by interposing zero readings and measurements of the intensity of the source. For smaller angles of deflexion it was found that the integrated intensity could be determined from a measurement of the blackening for the peak of the lines, multiplied by the average width as determined by measuring the area of the record. This of course implied that certain conditions as to the definition of the lines were satisfied. The justification for this procedure was derived from comparing the values obtained in this way with an actual integration of the X-ray intensities corresponding to the various parts of each line.

To ascertain whether the measurements were affected by the width of the slit, records with slits of 0·02 and 0·07 mm. were made. Fig. 1 shows the curves so obtained for the (222) and (422) reflexion plotted on different scales of ordinates in order to make the lines comparable. The contours are very similar and the peak values expressed by I I, where I_0 is the deflexion for "fog" outside the line

and I is the deflexion on the peak, are in both cases smaller with the wider slit, the reductions being in the ratio 1·16 and 1·17 respectively, showing that the relative values are practically unaffected by the width of the slit. The narrower slit was used in the measurement of the lines. The X-ray intensities were evaluated by blackening marks produced in the ordinary way. Kodak roll-films were used in preference to special X-ray films, and several films superposed in order to have a check for any inequality of the emulsion.

Fig. 1.



Photometry of (222) reflexion with wide slit (*a*) and with fine slit (*b*), and (422) reflexion with wide slit (*c*) and with fine slit (*d*).

The following tables give the results of the measurements in the form discussed above. Fig. 2 shows them in the form of a graph. The F values for the reflexions from a single crystal are revised F values for which I am indebted to Mr. R. W. James and Miss E. Firth, these values will be published shortly.

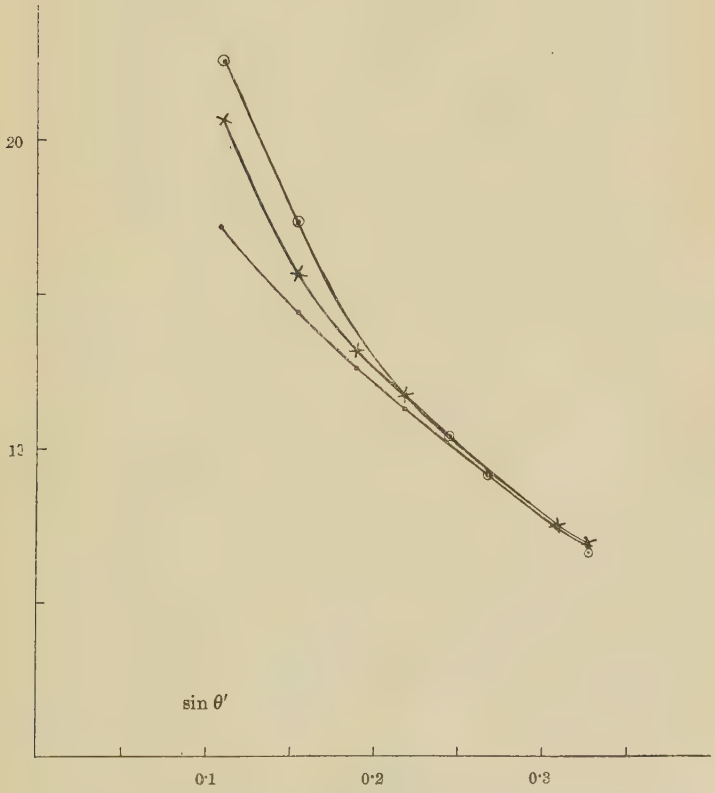
Reflexion from large crystal (James & Miss Firth).

Indices.	H^2.	F uncorrected.	F corrected for sec. extinction.	sin θ.
200	4	17·16	20·65	0·109
220	8	14·39	15·62	0·154
222	12	12·59	13·18	0·189
400	16	11·23	11·69	0·218
440	32	7·40	7·46	0·308
600	36	6·84	6·89	0·327

Reflexion from fine powder.

Indices.	H^2.	"Integrated" reflexion. P.	Multiplicity factor. p.	(rel. val.). F.	$\sin\theta$.	$\sin\theta'$.
200	4	18·3	3	22·6	0·273	0·109
220	8	9·61	6	17·4	0·386	0·154
420	20	2·33	12	10·4	0·611	0·244
422	24	1·54	12	9·16	0·699	0·267
442 (600)...	36	0·91	15	6·46	0·819	0·327

Fig. 2.



F values: ● from single crystal uncorrected.
× from single crystal corrected for secondary extinction.
○ from fine powder.

The F values obtained from the single crystal are absolute determinations, while our values obtained from the powder are relative values and are plotted in arbitrary units, so as

to obtain agreement for $\sin\theta = 0{\cdot}25$. For this angle the correction for secondary extinction as determined by Bragg becomes sufficiently small; it seems therefore best to make this point coincide in comparing the curves, as the determinations become less accurate for larger angles.

It will be seen that the values are in general in good agreement; for the deflexions at small angles, however, our values are slightly higher, indicating that the reflexions from large crystals were not quite free from primary extinction. Comparing the uncorrected values obtained from a single crystal with the values corrected for secondary extinction and with those obtained from the fine powder, it appears that primary extinction affects the reflexions from a large crystal to a much smaller degree than secondary extinction, for which allowance has been made.

The approximation between the values obtained from large crystals, comparatively coarse powders, and extremely small particles which very nearly satisfy the criterion of negligible secondary extinction show that in all these cases the crystal units are small.

Comparing this with the results obtained with other crystals possessing considerable primary extinction, it appears that rock-salt is an eminently suitable substance for intensity measurements.

To meet the more general case, the conditions for the reflexion of X-rays from powders indicate that in principle the best procedure for obtaining data on intensities consists in taking relative intensity measurements of reflexions from a powder layer of particles sufficiently small to satisfy Darwin's criterion for negligible primary extinction, satisfying thus very simple conditions for the interpretation of the results. If absolute measurements and therefore a comparison with the incident beam is required, the relation can be established by observing one reflexion from a single large crystal and determining the proper coefficient of absorption, using preferably a reflexion for which extinction is negligible.

It is not always easy to obtain powders of so small particles to satisfy the condition of negligible primary extinction, and evidence whether the mechanical treatment of grinding is sufficient to break the lattice into units much smaller than the dimensions of the particles seems not complete.

In the case of rock-salt the crystal units were evidently sufficiently small from the beginning, and the process of grinding, as carried out in the experiments of Havighurst,

was mainly required in order to produce particles small enough to eliminate secondary extinction in the individual particle.

In the case of gold, experiments of Dawson and the author showed that the mechanical treatment of filing was not sufficient to eliminate extinction, and similar conditions were observed by the author on calcite and on zinc carbonate powders, where considerable extinction was found after prolonged grinding. The same is borne out by experiments by Havighurst where exceptionally perfect crystals, obtained by a process of distillation, showed some primary extinction after grinding during several hours.

In conclusion the author wishes to express his thanks to Prof. W. L. Bragg, F.R.S., for expressing valuable criticisms in reading through the manuscript of this paper.

Physical Laboratories,
University of Manchester,
June 30th, 1927.

LIV. *The Flow of Heat in a Body generating Heat.* By J. H. Awbery, *B.A., B.Sc., Physics Department, National Physical Laboratory* *.

Abstract.

The flow of heat in a body in which heat is at the same time being generated is examined. The differential equation is set out, and forms of solution noted, for cartesian and for polar coordinates.

The problem of the temperature at all points and times, in a sphere generating heat, is solved in detail, when the constant initial temperature is given, the surface being held at a definite temperature from a time zero onwards, and also for the more elaborate case where the initial temperature distribution is an equilibrium one, and the boundary condition is Newton's law of cooling.

Introduction.

SINCE the publication of Fourier's pioneer treatise on the conduction of heat, the methods which he initiated have been applied to a multitude of problems, not only in heat conduction but in all branches of physics, particularly in the theory of the potential.

* Communicated by Sir J. E. Petavel, K.B.E., F.R.S.

In the theory of heat conduction, however, there are a series of problems to be considered, in which the body in which the heat-flow takes place is at the same time the seat of a continuous production of heat. The physical cases in which this occurs are somewhat limited, the most notable being those where an electric current is the source of the heat production; several such cases have been worked out, but, as far as the author is aware, only for the particular case of the steady state, in which the temperatures do not change with time, or else for the case of an infinite solid, with a plane face. Other cases in which conduction problems "with heat generation" have been solved have been dealt with by the method, due to Kelvin, of sources and sinks.

The purpose of the present paper is to examine briefly the modifications necessary to solve such cases analytically, and to give in detail the solution for a sphere.

Fundamental Equation.

By considering the net flow of heat into a small parallelopiped of sides dx, dy, dz, and equating it to zero, it is easily found that the fundamental differential equation of heat conduction takes the form

$$\mathrm{K}\left(\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}\right)=\rho\sigma\frac{\partial\theta}{\partial t}-\mathrm{Q},$$

where θ is the temperature at the time t and the point (x, y, z), K is the thermal conductivity, ρ and σ are the density and specific heat of the body, and Q the heat generated per second per unit volume of the body.

It will be convenient to use h^2 as a single symbol for $\mathrm{K}/\rho\sigma$, and b^2 for $\mathrm{Q}/\rho\sigma$, so that the equation takes the form

$$\frac{d\theta}{dt}=h^2\nabla^2\theta+b^2. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now, although this is not examined in the usual treatises, two cases of it have been thoroughly studied.

(*a*) When $b^2=0$, it becomes the usual "diffusion equation," and is known to have the useful solutions

$$\theta=\Sigma\mathrm{A}e^{mx+ny+pz+qt}, \quad \text{where} \quad h^2(m^2+n^2+p^2)=q,$$

and in which one or more of the exponents may be imaginary and take the form of trigonometrical functions.

(*b*) If $\dfrac{d\theta}{dt}=0$, we have the steady state, and the equation

is that known as Poisson's, considerably studied in electrostatics and gravitation, and, as mentioned above, amenable to treatment by Kelvin's method. One solution is

$$\theta = \mathrm{A} - \frac{b^2}{6h^2}(x^2+y^2+z^2).$$

In seeking solutions of the general equation (1), it is immediately evident that it cannot be simplified by the common device of assuming that there are solutions of the form (function of time) × (function of space coordinates), and in fact something of the nature of a particular integral is required.

The assumption that $\theta=\theta'+\theta''$, where $\frac{d\theta'}{dt} = h^2\nabla^2\theta'$ and $\frac{d\theta''}{dt} = 0$, leads to $h^2\nabla^2\theta''=b^2$, so that the solution may be taken as the sum of two others, one satisfying the Fourier, and the other Poisson's equation.

It follows that a solution of the equation (1) is

$$\theta = \mathrm{A} - \frac{b^2}{6h^2}(x^2+y^2+z^2) + \Sigma \mathrm{B} e^{mx+ny+pz+qt}, \quad . \quad (2)$$

with the same relation as before between m, n, p, and q.

It is evident that this form of solution is available to satisfy any set of boundary conditions for which the problem without heat generation is soluble by means of a series

$$\theta = \mathrm{A} + \Sigma \mathrm{B} e^{mx+ny+pz+qt},$$

i. e. for most cases whose solutions are known when $b=0$.

Spherical Polar Coordinates.

Turning now to the problems which are more suitably dealt with in polar coordinates, we shall restrict consideration to those where the heat-flow is uniform, so that the temperature is a function of the coordinate r, and independent of angular coordinates.

Either by transformation of the equation (1), or by considering the heat-flow into a spherical shell, the fundamental equation is shown to be

$$\frac{d\theta}{dt} = \frac{h^2}{r^2}\frac{d}{dr}\left(r^2\frac{d\theta}{dr}\right) + b^2. \quad . \quad . \quad . \quad . \quad (3)$$

Taking a new variable $u=r\theta$, this becomes

$$\frac{du}{dt}=b^2r+h^2\frac{d^2u}{dr^2},$$

which is satisfied by $u=u'+u''$

if $$u'=\mathrm{A}+\mathrm{B}r-\frac{b^2r^3}{6h^2}$$

and u'' satisfies $$h^2\frac{d^2u''}{dr^2}=\frac{du''}{dt},$$

the latter being identical in form with the Fourier equation.

Temperatures in a sphere, initially at θ_0, with its surface suddenly held at θ_1.

We may illustrate the use of these solutions by working out the above problem.

From the last equations we may take

$$u=\mathrm{A}+\mathrm{B}r-\frac{b^2r^3}{h^2}+\Sigma e^{-n^2h^2t}(\mathrm{C}\cos nr+\mathrm{D}\sin nr)$$

or

$$\theta=\frac{u}{r}=\frac{\mathrm{A}}{r}+\mathrm{B}-\frac{b^2r^2}{h^2}+\frac{1}{r}\Sigma e^{-n^2h^2t}(\mathrm{C}\cos nr+\mathrm{D}\sin nr).$$

To apply this to the particular problem, we must evidently take $\mathrm{A}=\mathrm{C}=0$, to avoid infinite temperatures at the centre of the sphere.

This gives, as the initial condition,

$$\theta_0=\mathrm{B}-\frac{b^2r^2}{6h^2}+\frac{1}{r}\Sigma\mathrm{D}\sin nr \quad . \quad . \quad . \quad (4)$$

for all values of r.

The surface condition, valid for all positive values of t, is

$$\theta_1=\mathrm{B}-\frac{b^2a^2}{6h^2}+\frac{1}{a}\Sigma\mathrm{D}e^{-n^2h^2t}\sin na.$$

We can comply with the latter equation by taking $na=m\pi$, where m is an integer, so that the sines vanish at $r=a$; then

$$\mathrm{B}=\theta_1+\frac{b^2a^2}{h^2},$$

and (4) becomes

$$\theta_0=\theta_1+\frac{b^2}{6h^2}(a^2-r^2)+\frac{1}{r}\Sigma\mathrm{D}\sin\frac{m\pi r}{a}$$

an equation for the coefficients D.

In fact, the D's are the coefficients in the Fourier sine series for

$$r(\theta_0-\theta_1)+\frac{b^2r}{6h^2}(r^2-a^2),$$

so that

$$D_m=\frac{2}{a}\int_0^a\left[r(\theta_0-\theta_1)-\frac{b^2a^2r}{6h^2}+\frac{b^2r^3}{6h^2}\right]\sin\frac{m\pi r}{a}dr.$$

The integrals of the form $Nr^3\sin\frac{m\pi r}{a}$ and of $Mr\sin\frac{m\pi r}{a}$ reduce by parts, and the terms involving sines vanish at both limits, so that D*m* reduces to

$$(-1)^m\left[\frac{2a^3b^2}{h^2m^3\pi^3}+\frac{2a(\theta_1-\theta_0)}{m\pi}\right], \quad . \quad . \quad . \quad (5)$$

and the *final equation for the temperature* is

$$\theta=\theta_1+\frac{b^2(a^2-r^2)}{6h^2}+\frac{1}{r}\Sigma D_m e^{-m^2\pi^2h^2t/a^2}\sin\frac{m\pi r}{a}, \quad . \quad (6)$$

with the above values of D_m.

As particular cases, we notice :

(1) When $t=0$, θ reduces to

$$\theta_1+\frac{b^2(a^2-r^2)}{6h^2}+\frac{1}{r}\Sigma D_m\sin\frac{m\pi r}{a},$$

and since the Fourier series is that of

$$r(\theta_0-\theta_1)+\frac{b^2r}{6h^2}(r^2-a^2),$$

this is θ_0 as it should be.

(2) When $t=\infty$,

$$\theta=\theta_1+\frac{b^2(a^2-r^2)}{6h^2},$$

showing what is the excess temperature at any point, after the steady state has been attained. It is also to be noted that at the surface this becomes simply θ_1, as it is by hypothesis at all times later than $t=0$.

Further, it is obvious that when $t=\infty$, the temperature gradient in the sphere is $\frac{-2b^2r}{6h^2}$, so that the heat-flow through

the surface, per second, being $-\mathrm{KS}\left(\frac{d\theta}{dr}\right)_a$, where S is the area, is

$$\frac{2b^2a\mathrm{K}}{h^2}.4\pi a^2=\frac{4}{3}\frac{b^2a^3\mathrm{K}}{h^2},$$

or, since $b^2=\mathrm{Q}/\rho\sigma$ and $h^2=\mathrm{K}/\rho\sigma$, the heat-flow is $\frac{4}{3}\mathrm{Q}a^3$, *i. e.* Q × volume of sphere, the result to be anticipated.

(3) When $r=a$, the sines vanish, and $\theta=\theta_1$ simply.

(4) When $r=0$, we have

$$\frac{1}{r}\sin\frac{m\pi r}{a}=\frac{m\pi}{a},$$

and θ takes the form

$$\theta_1+\frac{b^2a^2}{6h^2}+\Sigma\mathrm{D}_m.\frac{m\pi}{a}e^{-m^2\pi^2h^2t/a^2},$$

an expression for the excess at the centre at various times.

(5) When $b^2=0$, the problem simplifies to the case of no heat generation. D_m assumes the simple form $\frac{2a}{m\pi}(\theta_1-\theta_0)$, and θ is simply

$$\theta_1+\frac{2a(\theta_1-\theta_0)}{\pi r}\Sigma\frac{1}{m}e^{-m^2\pi^2h^2t/a^2}\sin\frac{m\pi r}{a}, \quad . \quad . \quad (7)$$

which is the form (slightly extended) usually given in the text-books *.

Numerical illustration.

The form of D_m is too complicated, and changes too much with variations in the relative values of b and h, to make it profitable to calculate an example fully. We may, however, calculate numerical values for the following problem (which in fact suggested the subject).

Apples when placed on shipboard are usually warm, and have to be cooled down to be carried in cold storage ; they also, by their respiration, generate heat. It is required to calculate to what extent they are warmer, after a given time in the refrigerated chamber, than they would be if they generated no heat. The theoretical answer to the latter problem is well known, so that this difference will complete the solution for the actual case. We assume that the apples are initially uniform throughout at θ_0, and that their skins

* See Carslaw, ' Heat Conduction,' Art. 64, or Byerly, ' Fourier Series and Integrals,' Art. 66.

assume the temperature θ_1 immediately they are introduced into the hold.

The excess temperature referred to is the difference between expressions (6) and (7), viz.,

$$\frac{b^2(a^2-r^2)}{6h^2}+\frac{1}{r}\Sigma(-1)^m\cdot\frac{2a^3b^2}{h^2m^3\pi^3}e^{-m^2\pi^2h^2t/a^2}\sin\frac{m\pi r}{a}.$$

Since the centre of each apple is at the highest temperature, the value there is the only one of interest in the practical problem, and at this point the excess is simply

$$\frac{b^2a^2}{6h^2}+\Sigma(-1)^m\cdot\frac{2a^2b^2}{h^2m^2\pi^2}e^{-m^2\pi^2h^2t/a^2}. \quad . \quad . \quad . \quad (8)$$

The following values were taken for the constants :—

a, the radius of an apple, $=4$ cm.,
$b^2=0{\cdot}0000133$ C.G.S. centigrade units,
$h^2=0{\cdot}00155$ C.G.S. centigrade units,

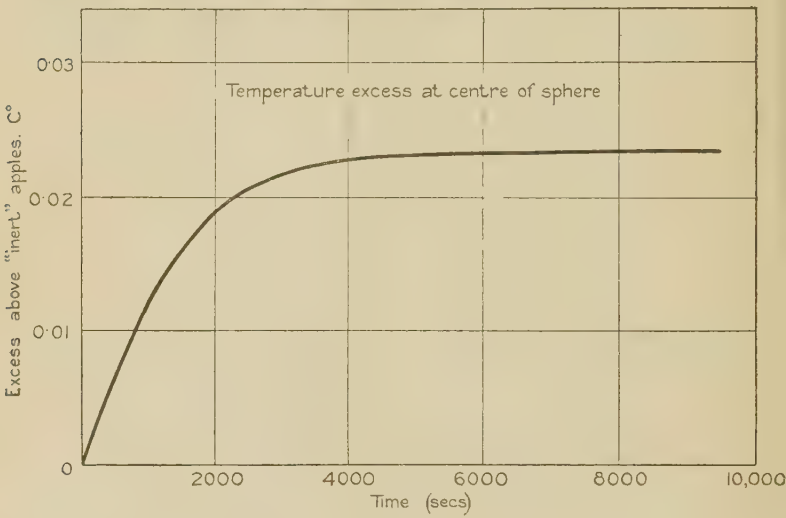
which leads to the following values, which are also plotted in the figure.

Time. (secs.)	Excess temperature at centre, above that of an apple generating no heat. (° C.)
0	0·0000
200	0·0027
400	0·0054
500	0·0067
600	0·0080
1000	0·0125
2000	0·0190
3000	0·0216
4000	0·0226
5000	0·0230
6000	0·0231
7000	0·0232
8000	0·0232
9000	0·0232
10000	0·0232

It is interesting to remark that the value 0·0000 at $t=0$ is a calculated one, the series in equation (8) being actually summed to 0·0232, the value of the first term. It thus provides an excellent check on the algebra and on the numerical work. Its meaning is, of course, that whether

there is heat generation or not, the initial temperature at the centre is assumed fixed at the same value.

As far as this particular problem is concerned, the net result is that the effect of heat generation is negligible. Nevertheless, it appears desirable to place the general equations on record, since it is easy to conceive of cases where the results of these calculations might be required.



Sphere cooling by radiation.

We pass to a second, more practical, problem. It was evident from the beginning that the assumption of a uniform initial temperature throughout was an artificial one, but the result of the previous problem for $t=\infty$ shows what distribution is to be taken, as representing an equilibrium condition. We may also replace the condition of constant temperature at the surface, by the assumption that the sphere loses heat to its surroundings at a rate proportional to the temperature excess above the air. The problem is therefore that of a sphere initially in a state such that its temperature is $\theta_1+\frac{b^2(a^2-r^2)}{6h^2}$. At a time zero it is placed in an enclosure at which it loses heat at a rate $\mathrm{E}(\theta_a-\theta_2)$ per sq. cm., E being its emissivity, and θ_a the (variable) surface temperature.

As before, the temperature may be taken as

$$\theta=\mathrm{B}-\frac{b^2r^2}{bh^2}+\frac{1}{r}\Sigma\mathrm{D}e^{-n^2h^2t}\sin nr,$$

so that expressions of the initial and boundary conditions are now

$$\theta_1 + \frac{b^2(a^2-r^2)}{6h^2} = \mathrm{B} - \frac{b^2r^2}{6h^2} + \frac{1}{r}\Sigma \mathrm{D} \sin nr, \quad . \quad . \quad (9)$$

$$-\mathrm{K}\left[-\frac{2b^2a}{6h^2} - \frac{1}{a^2}\Sigma \mathrm{D}e^{-n^2h^2t}\sin na + \frac{1}{a}\Sigma n \mathrm{D}e^{-n^2h^2t}\cos na\right]$$

$$= \mathrm{E}\left[\mathrm{B} - \frac{b^2a^2}{6h^2} + \frac{1}{a}\Sigma \mathrm{D}e^{-n^2h^2t}\sin na - \theta_2\right], \quad (10)$$

the latter expressing that $-\mathrm{K}\left(\frac{\partial\theta}{\partial r}\right)_a = (\theta_a - \theta_2)$, or that heat does not accumulate in the surfaee.

Equation (10) can only be satisfied if the constant terms, and those involving time, are equated separately.

Thus
$$\mathrm{B} = \frac{ab^2(\mathrm{E}a + 2\mathrm{K})}{6\mathrm{E}h^2} + \theta_2$$

$$\tan na = \frac{\mathrm{K}na}{\mathrm{K} - \mathrm{E}a}.$$

Thus

$n = \phi_m/a$, where ϕ_m is the mth root of $\tan\phi = \frac{\mathrm{K}\phi}{\mathrm{K} - \mathrm{E}a}$. (11)

Substituting these values in (9), it takes the form

$$\theta_1 = \frac{\mathrm{K}ab^2}{3\mathrm{E}h^2} + \theta_2 + \frac{1}{r}\Sigma \mathrm{D} \sin\frac{\phi r}{a},$$

or putting

$$\theta_1 - \frac{\mathrm{K}ab^2}{3\mathrm{E}h^2} - \theta_2 = a \text{ constant } \mathrm{F},$$

$$\Sigma \mathrm{D} \sin \phi r/a = \mathrm{F}r.$$

The series on the left is not a Fourier series, owing to the form of ϕ, but it is a series in which an arbitrary function may be expanded. In fact *

$$\mathrm{D} = \frac{2}{a}\left[\frac{\phi^2 + \left(\frac{\mathrm{E}a - \mathrm{K}}{\mathrm{K}}\right)^2}{\phi^2 + \frac{\mathrm{E}a(\mathrm{E}a - \mathrm{K})}{\mathrm{K}^2}}\right]\int_0^a \mathrm{F}r \sin\frac{\phi r}{a}\,dr$$

$$= \frac{2\mathrm{F}}{a}\left[\frac{\phi^2\mathrm{K}^2 + (\mathrm{E}a - \mathrm{K})^2}{\phi^2\mathrm{K}^2 + \mathrm{E}a(\mathrm{E}a - \mathrm{K})}\right]\left[\frac{a^2\sin\phi}{\phi^2} - \frac{a^2\cos\phi}{\phi}\right].$$

* See Byerly, *loc. cit.* p. 120.

Since $\tan\phi$ is $\frac{\mathrm{K}\phi}{\mathrm{E}-\mathrm{E}}$, this may be transformed into

$$\mathrm{D}=\frac{2a^2\mathrm{EF}}{\phi}\frac{[\phi^2\mathrm{K}^2+(\mathrm{E}a-\mathrm{K})^2]^{\frac{1}{2}}}{[\phi^2\mathrm{K}^2+\mathrm{E}a(\mathrm{E}a-\mathrm{K})]}, \quad . \quad . \quad (12)$$

and the final result is the following somewhat unwieldy one:

$$\theta=\frac{(a^2-r^2)b^2}{6h^2}+\frac{\mathrm{K}ab^2}{3\mathrm{E}h^2}+\theta_2+\frac{1}{r}\Sigma\mathrm{D}e^{-\phi^2h^2t/a^2}\sin\frac{\phi r}{a},$$

where the successive D's are given by equation (12), F being an abbreviation for $(\theta_1-\theta_2)-\frac{\mathrm{K}ab^2}{3\mathrm{E}h_2}$, and ϕ being given by the roots of equation (11).

It is difficult to devise checks on the algebra. If the series is correctly expanded, the solution gives the correct answer at $t=0$. At $t=\infty$ it shows an equilibrium condition in which the surface temperature exceeds the surroundings by $\frac{\mathrm{K}ab^2}{3\mathrm{E}h^2}$, and this leads, in fact, to a heat-loss per second equal to the rate of generation.

If $b=0$, not only is the heat-loss zero, but the initial temperature becomes the constant θ_1. In this case θ reduces to $\theta_2+\frac{1}{r}\Sigma\mathrm{D}e^{-\phi^2h^2t/a^2}\sin\frac{\phi r}{a}$, and D becomes

$$\frac{2a^2(\theta_1-\theta_2)}{\phi}\frac{[\phi^2\mathrm{K}^2+(\mathrm{E}a-\mathrm{K})^2]^{\frac{1}{2}}}{[\phi^2\mathrm{K}^2+\mathrm{E}a(\mathrm{E}a-\mathrm{K})]},$$

which agrees with the known result given in Byerly (*loc. cit.* p. 122).

LV. *Notices respecting New Books.*

Tungsten: a Treatise on its Metallurgy, Properties, and Applications. By Dr. Colin J. Smithells. Pp. viii+167, with 33 plates. (London: Chapman & Hall, Ltd. 1926. Price 21*s.* net.)

THE importance of tungsten for industrial purposes is due to two properties: its low vapour pressure at high temperatures, which makes it possible to take advantage of its high melting-point (which is exceeded only by that of carbon), and its power of hardening metals with which it is alloyed. Its chief uses are for making high-speed steels and for electric light and thermionic valve filaments. It is valuable also for galvanometer suspensions,

on account of its high elasticity, for targets in X-ray tubes, and for electrical contacts in motor-car magnetos, &c. Its properties are remarkable, and special methods have to be employed in working it. Although at room temperatures it is chemically inert, at high temperatures it is readily oxidizable, and in manufacturing processes or practical applications involving high temperatures it must be surrounded by an atmosphere of hydrogen or nitrogen.

In order to obtain tungsten in a ductile condition from the powdered metallic form in which it is initially obtained, it is first pressed into ingots by mechanical pressure; the ingots are then sintered in a furnace so as to be readily handled, formed by passing a heavy current through so as partially to eliminate the voids; swaged at high temperature by a mechanical hammering process, and finally drawn into wires by passing through a series of disks. The wires so obtained are essentially a bundle of crystalline fibres. On heating, recrystallization occurs and the ductility is lost.

Tungsten thus presents many problems of interest to the metallurgist and to the industrial user. Dr. Smithell's book deals with these problems in a very clear and interesting manner and is likely to form a standard work of reference on this subject. Detailed references to original publications are given. The book is well illustrated, and the numerous photo-micrographs may be particularly commended.

Lens Computing. By J. W. Gifford. (Macmillan & Co. 7*s* 6*d*.)

Colonel Gifford's book gives a short and concise account of lens computation by trigonometrical trace. After the introductory chapters on achromatism and spherical aberration, the method is applied to doublets and to various kinds of eyepieces—in particular, a modified Huyghenian eyepiece and a new triple erector. Several numerical examples are worked out in detail, including the traces of rays of a doublet and of an Apochromatic triple telescope object-glass.

Recent Developments in Atomic Theory. By C. G. Darwin. (Humphrey Milford, Oxford University Press. 1927. 1*s*. net.)

In this short lecture Prof. Darwin calls attention to three important developments in Atomic physics, the classical experiments of Gerlach and Stern, the rotating electron of Goudsmit and Uhlenbeck, and the Mechanics of Heisenberg for the study of atomic structure. "We hope that with the New Mechanics and the rotating electron a new era has set in which will found a true atomic mechanics."

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. III. Ti, Zr. Hf, Th, Ge, Sn, Pb, Inert Gases. By J. W. Mellor, D.Sc. Pp. x+977, with 255 diagrams. (London: Longmans, Green & Co. 1927. Price 63*s.* net.)

The seventh volume of Dr. Mellor's Comprehensive Treatise follows the same general lines as the earlier ones. For each element is given its history, occurrence, extraction, physical and chemical properties, valency and atomic weight, alloys, oxides, salts. At the end of each section detailed references are given to original publications. For lead alone these references total in all nearly 90 pages of close type, from which the thoroughness with which the author has examined chemical literature can be judged. Many of the references bear the date 1926, so that the present volume includes an account of the most recent work.

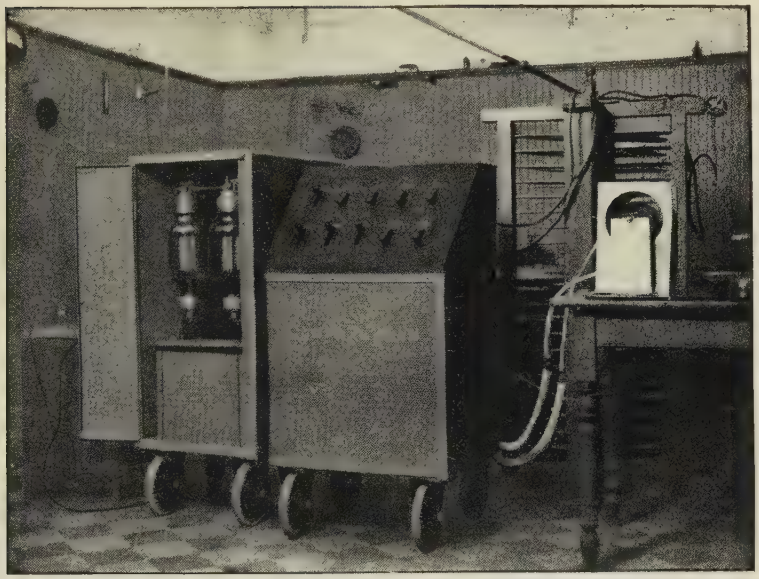
The compilation of such a treatise single-handed is a monumental piece of work; it is, however, more than a mere compilation, for the whole of the material is critically examined and welded together into a homogeneous whole. Dr. Mellor has placed all inorganic chemists under a debt of gratitude to him, and they will all hope that he will be able to carry his monumental task to completion.

Collected Papers of Sir James Dewar. Edited by Lady Dewar with the assistance of J. D. Hamilton Dickson, H. Munro Ross, and E. C. Scott Dickson. Two volumes: pp. xxii+1489, with two plates. (Cambridge University Press. 1927. Price £4 4*s.* net.)

In these two volumes are contained all the scientific papers and addresses by Sir James Dewar, together with papers published jointly with other investigators, excepting those in which he was associated with Professor G. D. Liveing. These have already been published in collected form. A few hitherto unpublished investigations are also included. Dewar was a great experimentalist, and in manipulative skill he had few equals. His own work lay largely in the borderlands of science; such as the liquefaction of gases, the production of low temperatures, the study of the properties of matter at such temperatures, high-vacuum technique, phosphorescence, soap-films. With theories he was less concerned. Theories must be built upon observation, but it is rarely that great experimental skill and a high power of theoretical interpretation are combined in the same person. These two volumes will prove of great interest to both categories of investigators; in particular, Dewar's experiments which have a bearing upon inter-molecular forces must prove of great value for the formulation of a theory of such forces. The volumes form a fitting tribute to a long life's work. A name index and a detailed subject index are given at the end of the second volume.

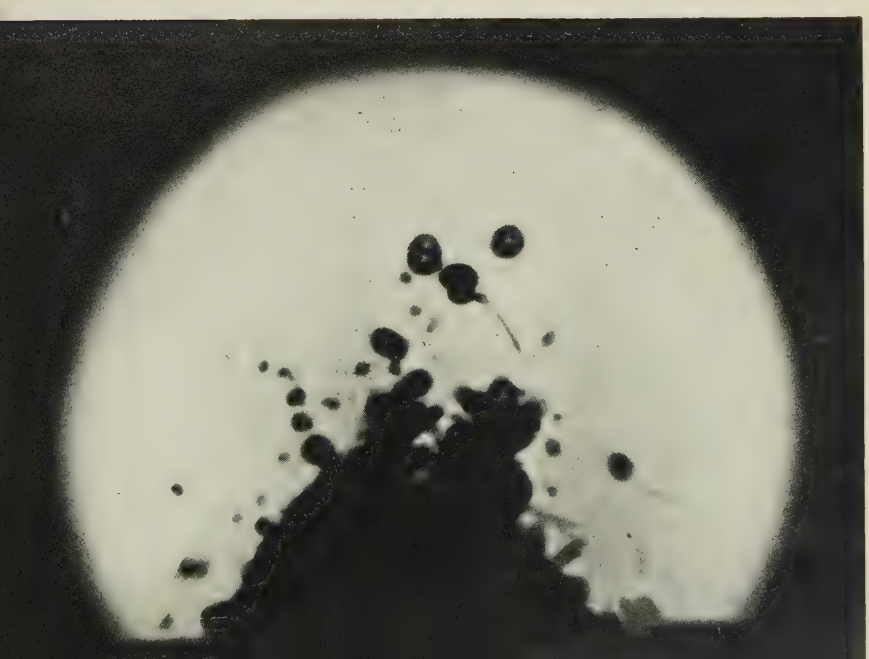
[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

Fig. 1.



Two 1000 Watt tubes. Oil condensers. Variable air condenser and coils.

Fig. 2.



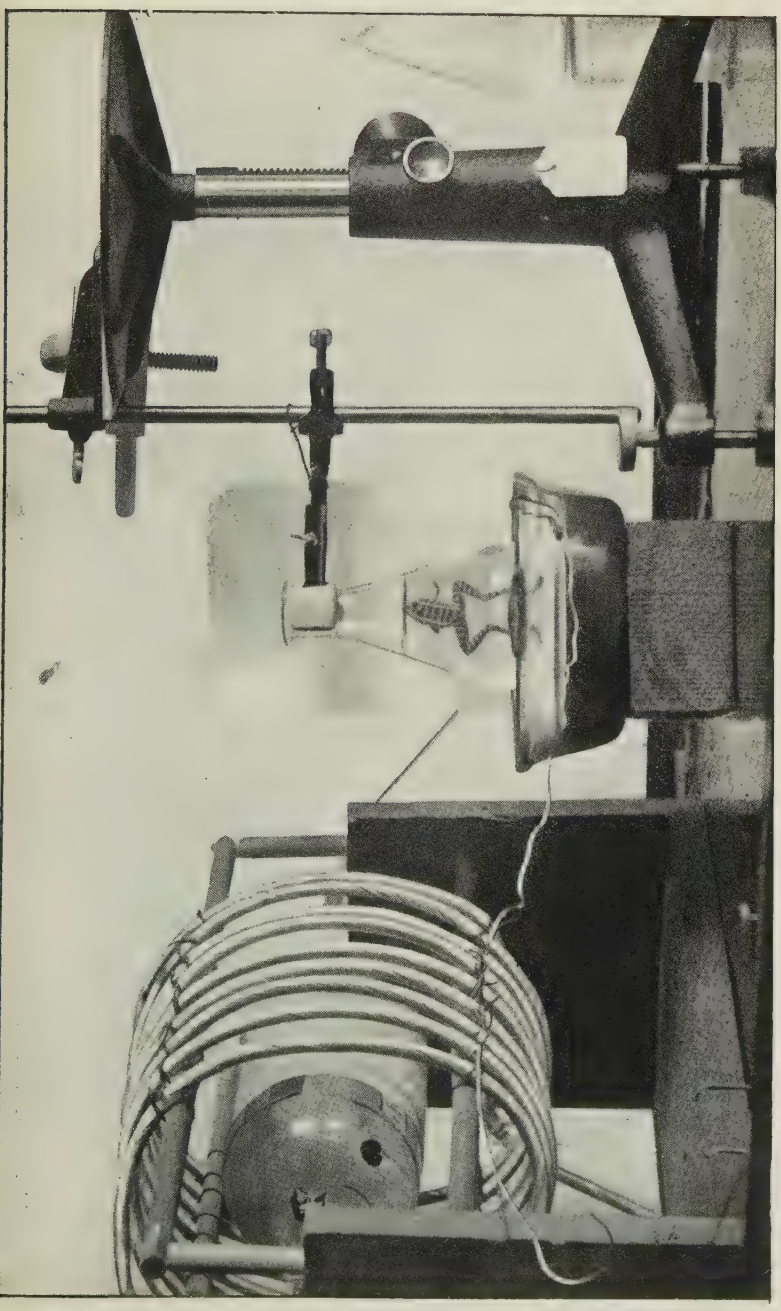
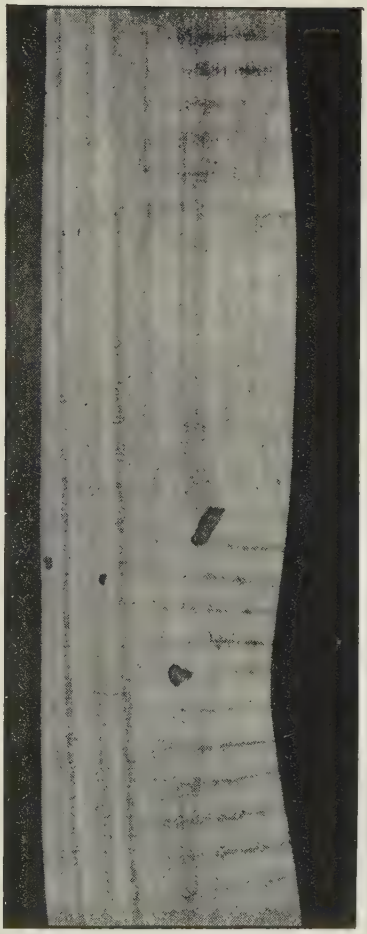
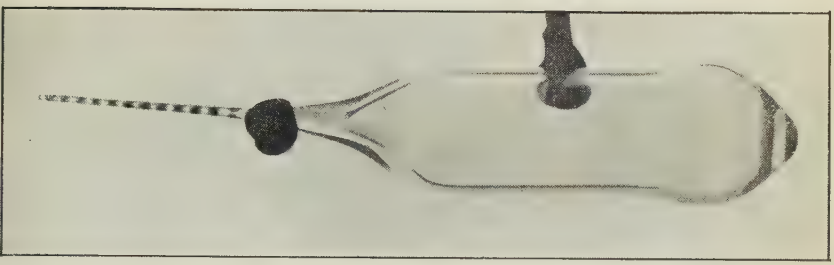


Fig. 3.

Fig. 4.





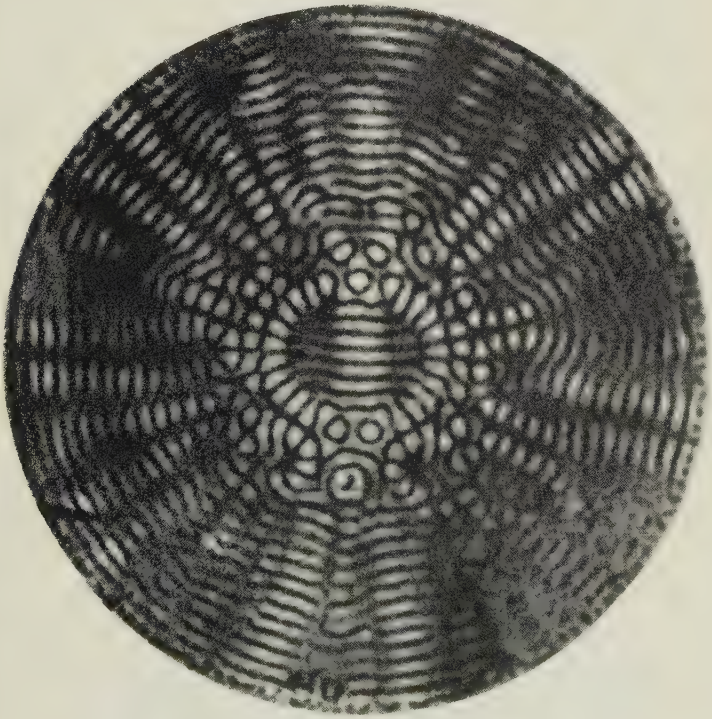


Fig. 5.

Fig. 7.

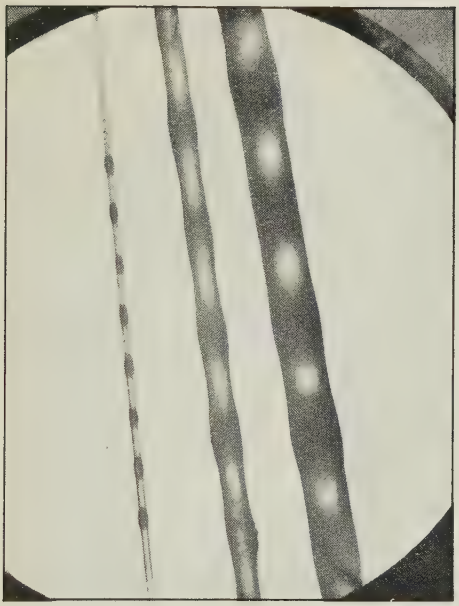


Fig. 8.

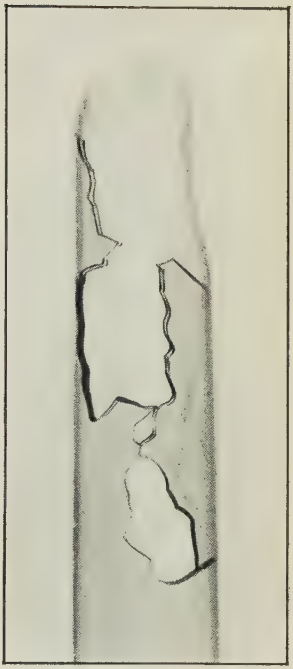


Fig. 9.

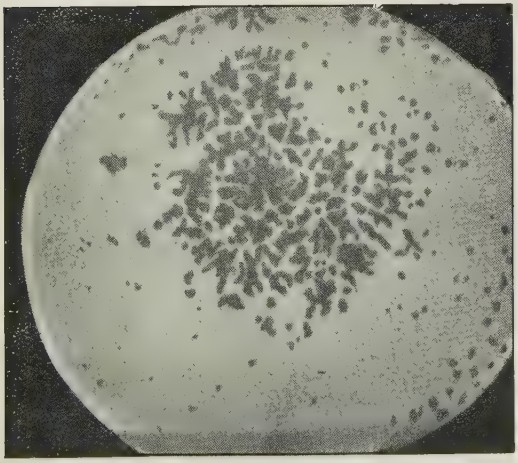


Fig. 10.

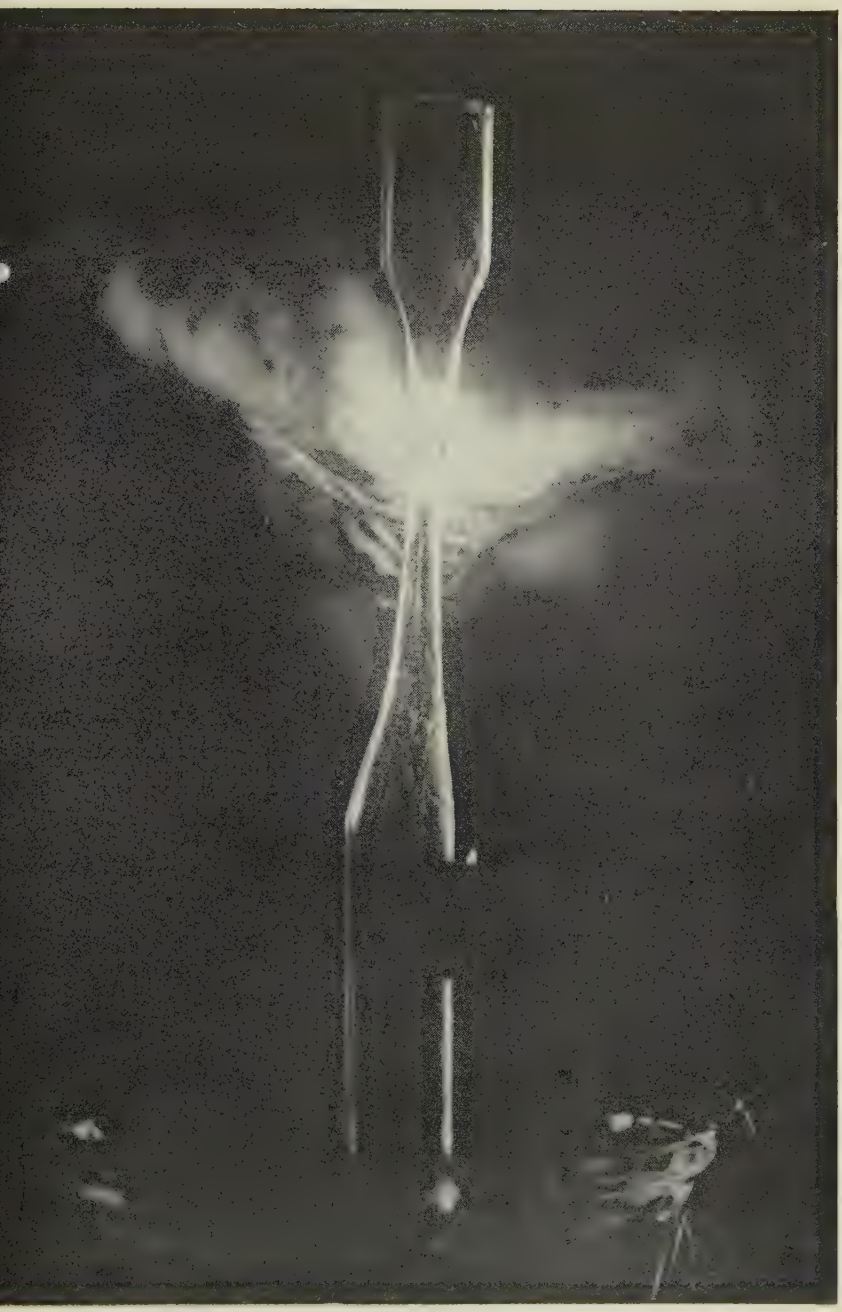


Fig. 3.

Fig. 1.

Fig. 2